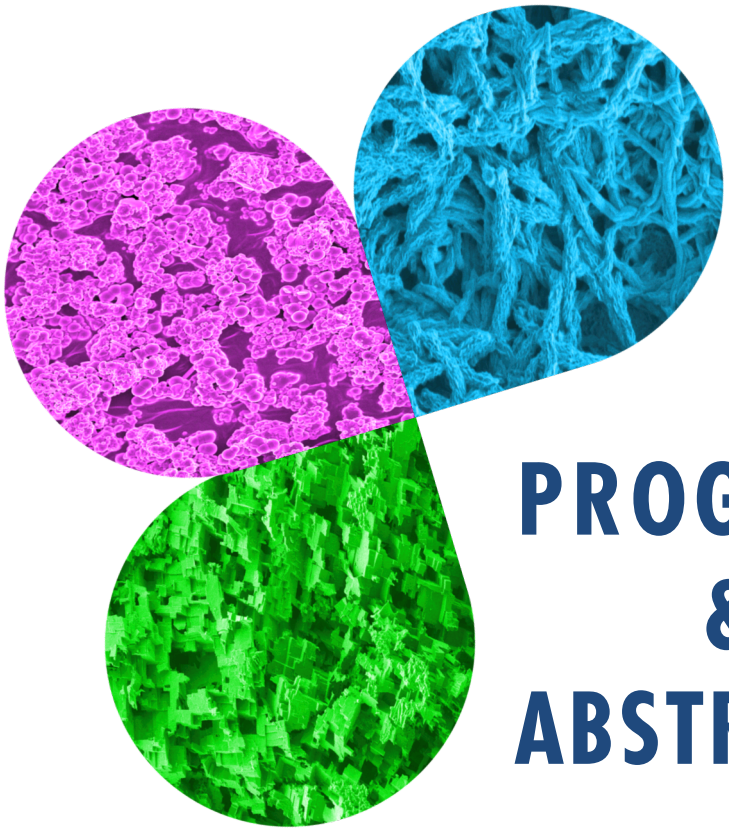
Superhydrophobic/superoleophobic surfaces based on conducting polymers

Thierry Darmanin, Frédéric Guittard

INTERNATIONAL CONFERENCE

on Bioinspired and Biobased Chemistry & Materials

October 3-5, 2012



PROGRAM & ABSTRACTS

MRS Materials Research Society

www.nice-conference.com

CONTENTS

Dear Delegates,
Dear Colleagues,

It is our great honour and privilege to welcome you to Nice (France) for the first international conference on Bioinspired and Biobased Chemistry & Materials from 3rd to 5th October 2012. “Nice” as “Nature Inspires, Chemistry Engineers” is also the acronym of the thematic of this conference.

I would like to thank all delegates, all speakers and poster presenters, coming from all over the world, to communicate the latest exciting developments and results in the dynamic fields of Materials and Chemistry and will turn that conference into an exciting and successful event. The intention is to provide a dynamic platform for academic colleagues or industrial partners but also to give an intimate environment in order to stimulate ideas or to start collaborative projects, in a scientific field which impacts so importantly on the future.

The entire organizing committee has put in months of valuable efforts for your service and for the quality of scientific speakers. We hope you will find the meeting scientifically stimulating and thought-provoking for new projects. If you need anything further, do not hesitate to contact me or any other member of the conference team.

Yours,

Frederic GUITTARD
Chair – N.I.C.E. 2012 conference

INTERNATIONAL SCIENTIFIC COMMITTEE

Michele Aresta (University of Bari, Italy)
Alfons Baiker (Institute for Chemical and Bioengineering, Switzerland)
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Ulrich Schubert (Friedrich-Schiller-Universität, Germany)
Vladimir V. Tsukruk (School of Material Science and Engineering School of Polymer, U.S.A.)
Dean C. Webster (Department of Polymers and Coatings, North Dakota State University, U.S.A.)
Francoise M. Winnik (Excecutive Editor, Langmuir, Canada)
Xi Zhang (Senior Editor, Langmuir, China)

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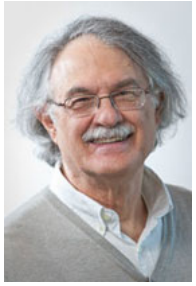
Abdoulaye Drame
Gennifer Padoan
Matthieu Sonnati
Elisabeth Taffin de Givenchy
Jeanne Tarrade
Mélanie Wolfs
Arnaud Zenerino

Main Speakers

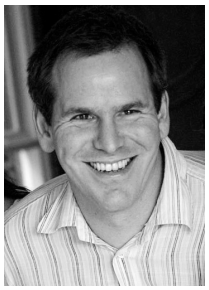
PLENARY SPEAKERS



PL1: Georges Belfort, Rensselaer Polytechnic Institute, U.S.A.

Transport though the Nuclear Pore Complex: Mechanistic Ideas and Development of an Artificial Nano-Selective Filter

Dr. Georges Belfort. Institute (Endowed) Professor at Rensselaer Polytechnic Institute Troy, NY, USA, the oldest non-military technical university in the English speaking world. He received his BS degree in Chemical Engineering at the University of Cape Town, South Africa and MS and PhD in Engineering from University of California, Irvine, USA. He has broad research interests include biomolecular separations (filtration, biofuels, leveraging rDNA with inteins), interfacial science (proteins at interfaces, high throughput surface modification), mass transfer and fluid mechanics, protein misfolding (amyloid aggregation) and kinetics, single molecule force spectroscopy, nature inspired separation (nuclear pore complex). He has received awards in the USA on Separations (ACS (1995) and AIChE (2000)), the ACS Murphree Award in Industrial and Engineering Chemistry (2008) and the Alan S. Michaels Award “Recovery of Biological Molecules” ACS BIOT Div. Award, Anaheim, CA (2011), and is one of the "100 Chemical Engineers of the Modern Era" as part of the AIChE Centennial Celebration in 2008. He was elected a member of the US National Academy of Engineering, February 2003, appointed Member of the Scientific Advisory Board, Max Planck Institute for Dynamic Complex Technical Systems, Magdeburg, Germany, April 2011, and inducted as Foreign Corresponding Member of the Academy of Sciences of Bologna Institute, Class of Physical Sciences, Section of Technical Sciences, March 2012.



PL2: Nicolas H. Voelcker, University of South Australia 1, Australia

Nanomaterials Engineering with Diatoms

Professor Nicolas Voelcker. After completing his BSc at the University of Saarland (1993) and his MSc at the RWTH Aachen (1995) in Germany, Nico did his PhD thesis (1999) in polymer surface chemistry at the German Wool Research Institute under Professor Hartwig Höcker. He received postdoctoral fellowships to work in the area of bioorganic chemistry under Professor Reza Ghadiri at the Scripps Research Institute in La Jolla, California. In 2001 he became a Lecturer at Flinders University, an Associate Professor in 2006 and a full Professor in 2008. From 2008-2011, he was the Associate Head of the Faculty of Science and Engineering at Flinders University. Since 2012, he is a Professor in Chemistry and Materials Science at the Mawson Institute of the University of South Australia.

His key research interest lies in the fabrication and surface modification of porous materials for applications in biosensors, biochips, biomaterials and drug delivery. A core research activity in his laboratory is the study of porous silicon based nanostructures. Indeed, his laboratory is world leading in the field of porous silicon research as reflected by his publications and invitations to present at international meetings on porous semiconductor research. He has generated porous silicon based nanostructures to fabricate biosensors and chips for the high sensitivity detection of disease markers, genetic information, environmental toxins and drugs He has also pioneered the use of porous silicon as a scaffold for tissue engineering.

Using modern surface analytical spectroscopy and microscopy techniques, his research has also contributed to the understanding of the fundamental principles of interfacial interactions of proteins, nucleic acids and whole cells on solid surfaces. Using this fundamental understanding, he is also developing new nanostructured materials for biosensors, biochips, biomaterials and drug delivery.

He has authored well over 170 peer-reviewed journal articles. He has received fellowships from the German Research Foundation (DFG), the CSIRO, the Alexander von Humboldt Foundation and is a recipient of the Tall Poppy Science Award.

PL3: Bai Yang, Jilin University, P.R. China

Responsive Polymer Hybrid Materials Based on Bio-Inspired Micro- and Nano-Ordered Structures

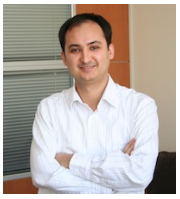
Bai Yang received his PhD in Polymer Chemistry and Physics in 1991 from Jilin University (China) working on the design and synthesis of high performence optical polymer and then going on the preparation of polymer nanocomposites and hybrids with high refractive index and photo-electro functionalities. He is associate professor since 1992 and promote to full professor since 1994. In 1999 he received the Outstanding Youth Fund from NSFC and the honors of Chenug Kong Scholar from the Ministry of Education of China.

His current research interests are focused on the synthesis and property studies of QDs in polymer; In situ compositing of nanoparticles in polymer matrix and high index optical hybrids; the fabrication of ordered polymeric microstructures for photonic properties by a modified soft lithography, including the new approaches to the syntheses of polymeric microspheres and inorganic nanoparticles; nano-micro scale fabrication of 2D ordered arrays by patterned surface induced wetting/dewetting process; structure controlled construction of 3D colloidal crystal via polymer-assistant lift-up soft lithography and modified μCP and self-assembling of organic and inorganic microspheres.

KEYNOTE SPEAKERS

Session A

KNA1
Lei JIANG
Chinese Academy of Sciences



KNA2
Mustafa O. GULER
Bilkent University

KNA3
Olli IKKALA
Aalto University

KNA4
Richard J. SPONTAK
North Carolina State University

KNA5
Abraham MARMUR
Technion – Israel Institute of Technology

KNA6
Jas Pal BADYAL
Durham University

KNA7
Russell J. STEWART
Department of Bioengineering

KNA8
Jim de YOREO
Lawrence Berkeley National Laboratory

KNA9
Kock-Yee LAW
Xerox Corporation

KN10
Anupama SHARMA
Panjab University

KNA11
Hu YAN
Zhengzhou University

KNA12
Xuehong LU
Nanyang Technological University

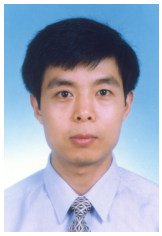
KNA13
Vadim G. KESSLER
Swedish University of Agricultural Sciences

KNA14
Thomas SCHEIBEL
Universität Bayreuth

KNA15
Mir Wais HOSSEINI
Université de Strasbourg

KNA16
Cordt ZOLLFRANCK
Technische Universität München

KNA17
Silvia VIGNOLINI
University of Cambridge



KNA18
Yanlin SONG
Chinese Academy of Sciences

Session B

KNB1
Yves QUENEAU
Université de Lyon

KNB2
Tongxiang FAN
Shanghai Jiaotong University

KNB3
Valentine I. VULLEV
University of California

KNB4
Anna TAMPIERI
ISTEC-CNR

KNB5
Vladimir V. TSUKRUK
Georgia Institute of Technology

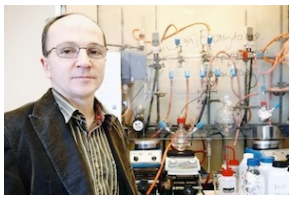
KNB6
Rachel MEALLET-RENAULT
ENS Cachan

KNB7
Sam P. de VISSER
University of Manchester

KNB8
Jackie Y. YING
Institute of Bioengineering and Nanotechnology

KNB9
Francesco CIARDELLI
IPCF-CNR

KNB10
Dominique MANDON
Institut de Chimie de Strasbourg



KNB11
Henri CRAMAIL
Université de Bordeaux

KB12
Karsten HAUPT
Université de Technologie de Compiègne

KNB13
Raz JELINEK
Ben Gurion University

KNB14
Rüdiger KNIEP
Max-Planck-Institute for Chemical Physics of Solids

KNB15
Pierre-J. LUTZ
Institut Charles Sadron

KNB16
Christopher K. OBER
Cornell University

KNB17
Bas de BRUIN
University of Amsterdam

KNB18
Tao DENG
Shanghai Jiao Tong University

SCIENTIFIC PROGRAM

October 3rd (Wednesday)

Registration 7:30-8:30 (Belvédère)

Welcome & Opening 8:30-9:00 (Théâtre)

Chairman: Rüdiger Kniep
PL1 9:00-9:40 Plenary (Théâtre)
Transport though the Nuclear Pore Complex: Mechanistic Ideas and Development of an Artificial Nano-Selective Filter
Georges Belfort
Rensselaer Polytechnic Institute, USA

Session A-I (Théâtre)
Chairman: Russel Stewart

KN A1 9:45–10:10 Keynote
Bio-Inspired, Smart, Multiscale Interfacial Materials
Lei Jiang
Chinese Academy of Sciences, P. R. China

KN A2 10:10–10:35 Keynote
Surface-Adhesive and Bioactive Self-Assembled Peptide Nanofibers for Bioinspired Functionalization of Metal Surfaces
Mustafa O. Guler
Bilkent University, Turkey

OR A1 10:35–10:50
Bioinspired Multi-Functional Coatings: Combining Surface Chemistry and Topology
Catarina Esteves
Eindhoven University of Technology, The Netherlands

Session B-I (Salle des Actes)
Chairman: Rüdiger Kniep

KN B1 9:45–10:10 Keynote
A Biomimetic Approach towards New Pseudo Glycoconjugates for Supramolecular Applications
Yves Queneau
Université de Lyon, France

KN B2 10:10–10:35 Keynote
Bioinspired Materials Derived from Natural Species
Tongxiang Fan
Shanghai Jiaotong University, P. R. China

OR B1 10:35–10:50
Bioinspired Enzyme Cascades
Herman S. Mansur
Federal University of Minas Gerais, Brazil

Pause 10:50–11:15

Session A-II (Théâtre)
Chairman: Vadim G. Kessler

KN A3 11:15–11:40 Keynote
Biomimetic Nanocomposites by Self-Assembly
Olli Ikkala
Aalto University, Finland

KN A4 11:40–12:05 Keynote
On the Versatility of Silk Fibroin as a Designer Polymer
Richard J. Spontak
North Carolina State University, USA

Session B-II (Salle des Actes)
Chairman: Georges Belfort

KN B3 11:15–11:40 Keynote
The Broad Impact of Biological Inspiration: from Sustainable Energy to Healthcare
Valentine I. Vullev
University of California, USA

KN B4 11:40–12:05 Keynote
Intelligent Bio-Materials for Tissue Engineering and Nanomedicine
Anna Tampieri
ISTEC-CNR, Italy

Session A-II (Théâtre)

OR A2 12:05–12:20
Reactive Monolayers: Templates for Biomolecules and Interfaces for Technology
Jurriaan Huskens
University of Twente, The Netherlands

OR A3 12:20–12:35
A New ALS Type Multi-Responsive Low-Molecular-Weight Organogel Based on Salicylidene Schiff Base
Shimei Jiang
Jilin University, P. R. China

OR A4 12:35–12:50
Elaboration and Rheological Study of Magnetic Sensitive Nanocomposites Biopolymer Based Networks
Alain Ponton
Université Paris Diderot, France

OR A5 12:50–13:05
Biomimetic $CaCO_3$ Mineralization Mediated by Hyperbranched Polymers: Morphology Evolution and Polymorphic Transformation
Dongzhong Chen
Nanjing University, P. R. China

Session B-II (Salle des Actes)

OR B2 12:05–12:20
Furan Modified Methacrylate Hydrogels through Diels-Alder Cycloaddition in Aqueous Media
Clara García-Astrain
University of the Basque Country, Spain

OR B3 12:20–12:35
Bio-Inspired Adhesive Materials for Cell-Based Cancer Diagnostics
Shutao Wang
Chinese Academy of Sciences, P. R. China

OR B4 12:35–12:50
Tunable, Dynamic and Electrically Stimulated Lectin-Carbohydrate Recognition on a Glycan-Grafted Conjugated Polymer
Shyh-Chyang Luo
RIKEN Advanced Science Institute, Japan

OR B5 12:50–13:05
Electrochemical Approach for Superoleophobic Surfaces
Hervé Bellanger
Nice-Sophia Antipolis University, France

Lunch 13:05–14:35

Session A-III (Théâtre)
Chairman: Mustafa O. Guler

KN A5 14:35–15:00 Keynote
Super-Hydrophobicity and Super-Hygrophobicity: in Air, under a Liquid, on a Liquid
Abraham Marmur
Technion – Israel Institute of Technology, Israel

OR A6 15:00–15:15
Reversible Switching between Superhydrophobic States on a Hierarchically Structured Surface
Robin H. A. Ras
Aalto University, Finland

OR A7 15:15–15:30
Orthogonal Mussel Inspired Surface Modification
Anja S. Goldmann
Karlsruhe Institute of Technology, Germany

OR A8 15:30–15:45
Hygroscopic Movement in Geraniaceae – Diversity, Structure and Evolution
Yael Abraham
Hebrew University of Jerusalem, Israel

Session B-III (Salle des Actes)
Chairman: Henri Cramail

KN B5 14:35–15:00 Keynote
Cell Surface Engineering with Synthetic and Natural LbL Nanoshells
Vladimir V. Tsukruk
Georgia Institute of Technology, Atlanta, USA

OR B6 15:00–15:15
Oxidation of Glucose Combined with Enzymatic Dioxygen Reduction in Biofuel Cells for Sustainable Energy Production
Sophie Tingry
Université Montpellier 2, France

OR B7 15:15–15:30
Bioinspired Encapsulation of Living *Chlorella* Cells within Protective and Functionalizable Silica/Titania Artificial Shells
Eun Hyea Ko
KAIST, Republic of Korea

OR B8 15:30–15:45
A Role for Polymer Brushes in Biosensors
M. Elizabeth Welch
Cornell University, USA

Session A-III (Théâtre)

OR A9 15:45–16:00
In-situ X-Ray Diffraction Experiments of Amyloidic Systems on Lotus-Leaves-Like Artificial Superhydrophobic Surfaces
Angelo Accardo
Istituto Italiano di Tecnologia, Italy

OR A10 16:00–16:15
A Description of Hairy, Ornamented and Glabrous Crab Shells (Brachyura) with a Discussion of their Biomimetic Possibilities
Fernando J. Parra-Velandia
National University of Singapore, Singapore

OR A11 16:15–16:30
Bioinspiration in the Field of Self-Healing Materials
Alain Périchaud
Catalyse company, France

OR A12 16:30–16:45
Self-Healing Polymers Based on Sol-Gel Chemistry
Mina Abdolah Zadeh
Delft University of Technology, The Netherlands

Session B-III (Salle des Actes)

KN B6 15:45–16:10
Self-Assembled Micellar Fluorescent Nanoobjects for Bioimaging Applications

Rachel Méallet-Renault

ENS Cachan, France

OR B9 16:15–16:30
The Design of 3D Liver Models Using Biopolymer Based Polyelectrolyte Multilayers
Padmavathy Rajagopalan
Virginia Tech, U.S.A.

OR B10 16:30–16:45
Bacteria-Templated Synthesis of Hollow Nanostructures
Liguo Hu
Shanghai Jiaotong University, P.R. China

Pause 16:45-17:00
Departure to the gala dinner (Registration required) 17 :00

October 4th (Thursday)

Chairman: Valentine I. Vullev
PL2 8:30-9:10 Plenary (Théâtre)
Nanomaterials Engineering with Diatoms
Nicolas H. Voelcker
University of South Australia 1, Australia

Session A-IV (Théâtre)
Chairman: Nicolas H. Voelcker

KN A6 9:15–9:40 Keynote
Functional Nanocoatings for Surface Biomimetics
Jas Pal Badyal
Durham University, UK

KN A7 9:40–10:05 Keynote
Sandcastle Worms and Caddisfly Larva: Inspiring New Biomaterials through Co-Polyelectrolyte Condensation
Russell J. Stewart
Department of Bioengineering, USA

OR A13 10:05–10:20
Extreme Wettability and Tunable Adhesion: Biomimicking beyond Nature?
Feng Zhou
Chinese Academy of Sciences, P. R. China

OR A14 10:20–10:35
Strong Dry Adhesives via Buckling-Based Interlocking
Shu Yang
University of Pennsylvania, USA

OR A15 10:35–10:50
Size Dependence Study on the Superhydrophobicity from Raspberry-like Silica Particles
Camille Carcouët
Eindhoven University of Technology, The Netherlands

Session B-IV (Salle des Actes)
Chairman: Valentine I. Vullev

KN B7 9:15–9:40 Keynote
Reactivity and Chemical Properties of Metal-Oxo Corroles: how do They Compare to Porphyrins?
Sam P. de Visser
University of Manchester, UK

KN B8 9:40–10:05 Keynote
Nanocomposite Design of Advanced Multifunctional Biomaterials
Jackie Y. Ying
Institute of Bioengineering and Nanotech., Singapore

KN B9 10:05–10:30
New Functional and Smart Materials through Molecular Modification and Blending of Biorelated Polymers
Francesco Ciardelli
IPCF-CNR, Italy

OR B11 10:35–10:50
Design of Functional Bio-Based Polyesters
Valérie Langlois
Institut de Chimie et des Matériaux Paris Est, France

Pause 10:50–11:15

Session A-V (Théâtre)
Chairman: Thomas Scheibel

KN A8 11:15–11:40 Keynote
Pathways of Matrix Protein Self-Assembly and Subsequent Mineral Nucleation
Jim De Yoreo
Lawrence Berkeley National Laboratory, USA

Session B-V (Salle des Actes)
Chairman: Bas de Bruin

KN B10 11:15–11:40 Keynote
Biomimetic Activation of Molecular Oxygen by Non-Heme Fe(II) Complexes with Tripodal Nitrogen Ligands: a Fundamental Approach
Dominique Mandon
Institut de Chimie de Strasbourg, France

Session A-V (Théâtre)

OR A16 11:40–11:55
Self-Organized Supramolecular Strategy towards Controlled Synthesis of Nano-Structured Silica Materials
Ren-Hua Jin
Kanagawa University, Japan

OR A17 11:55–12:10
Ice Templating: a Bioinspired Processing Route for Porous Materials
Sylvain Deville
Laboratory of Synthesis and Functionalization of Ceramics, France

OR A18 12:10–12:25
Synthesis of Hierarchical TiO_2 Nanostructures using Cotton and Ferula as a Chemical Reagent and a Template
Bruno Boury
Université Montpellier 2, France

OR A19 12:25–12:40
Biologically Inspired Processing of Metal Oxide Materials
David Wright
Vanderbilt University, USA

OR A20 12:40–12:55
Synthesis of Hollow Silica Particles via a Biosilification like Etching Process
Kai Zhang
Jilin University, P. R. China

OR A21 12:55–13:10
Cellulose Nanocrystal Reinforced Highly Elastic Rubber Composites
Henna Rosilo
Aalto University, Finland

Session B-V (Salle des Actes)

OR B12 11:40–11:55
Iron-Based Biomimetic Hybrid Materials for Catalytic Applications
Maria Louloudi
University of Ioannina, Greece

OR B13 11:55–12:10
A Biologically Inspired Copper/Topaquinone-like Dual Catalytic System for the Chemoselective Aerobic Oxidation of Amines to Imines
Martine Largeron
Université Paris Descartes, France

OR B14 12:10–12:25
Study of Hybrid Film Containing Peptide Nanostructures and Copper Complex(II) for Electroanalyticals Determinations
Wendel Andrade Alves
Universidade Federal do ABC, Brazil

OR B15 12:25–12:40
Synthesis of Hydrophobic Starch using Catalytic Approach
Catherine Pinel
IRCELYON, France

OR B16 12:40–12:55
Microbial Plastic Factory: New Lactate-Based and Related Biopolymers
Seiichi Taguchi
Hokkaido University, Japan

OR B17 12:55–13:10
Synthesis of Biobased Building Blocks from Vegetable Oils: toward Platform Chemicals
Sylvain Caillol
Ecole Supérieure de Chimie de Montpellier, France

Lunch 13:10–14:40

Session A-VI (Théâtre)
Chairman: Abraham Marmur

KN A9 14:40–15:05 Keynote
Design, Surface Properties and Applications of Robust Superoleophobic Surfaces
Kock-Yee Law
Xerox Corporation, USA

OR A22 15:05–15:20
Bio-Inspired Chitin-Oxide Nanocomposites through Self-Assembly
Bruno Alonso
Institut Charles Gerhardt, France

Session B-VI (Salle des Actes)
Chairman: Christopher K. Ober

KN B11 14:40–15:05 Keynote
Vegetable-Based Building Blocks for the Synthesis of Renewable Polymers
Henri Cramail
Université de Bordeaux, France

OR B18 15:05–15:20
Bio-Inspired Cationic Polymerization of Isoprene and Analogues
Frédéric Peruch
Université de Bordeaux, France

Session A-VI (Théâtre)

OR A23 15:20–15:35
Light Triggered Gelation and Adhesion by using Caged Marine Adhesive Protein Mimetic Polymer
Jin Nishida
Kyushu University, Japan

OR A24 15:35–15:50
Various Controlled ZnO Micro- and Nano-Structures: Morphologies Controlled, Wettabilities and Mechanical Properties
Zhiguang Guo
Chinese Academy of Sciences, P. R. China

OR A25 15:50–16:05
Anisotropic Wetting on Directional Gold Nanowires
Erhan Piskin
Hacettepe University, Turkey

OR A26 16:05–16:20

Self-Healing Thermal Conductive Adhesives

Ugo Lafont
Delft University of Technology, The Netherlands

OR A27 16:20–16:35
Polypeptide-Polystyrene Miktoarm Star Copolymers: Control of Self-Assembly by Polypeptide Arms
Susanna Junnila
Aalto University, Finland

Session B-VI (Salle des Actes)

OR B19 15:20–15:35
Green Chemistry: Bio-Based Renewable Materials
Avtar S. Matharu
University of York, UK

OR B20 15:35–15:50

Direct Conversion of Native Lignin to Functionality Controllable Polymers

Masamitsu Funaoka
Mie University, Japan

OR B21 15:50–16:05
Chitosan-Olive Oil Films Modified with Cellulose Nanocrystals
Mariana Pereda
Grenoble Institute of Technology, France

OR B22 16:05–16:20
Fluorous-Modified Natural Surfactants as Compatibilizers for Fluorinated Phases and Materials
Roberto Milani
VTT Technical Research Centre of Finland, Finland

OR B23 16:20–16:35

New Biomimetic Surface Treatment Based on Saponified Vegetal Oil

Delphine Veys-Renaux
Université de Lorraine, France

Pause 16:35–17:00

Session A-VII (Théâtre)
Chairman: Richard J. Spontak

KN A10 17:00-17:25
Bio-nanocomposites based on Cellulose Nanofibers (from Agricultural Biomass) Reinforced in Thermoplastic Starch Polymer
Anupama Sharma
Panjab University, India

OR A28 17:25–17:40
Development of Chitosan Based Microcapsules by Electrostatic Layer by Layer Method to Encapsulate Lignans for Textile Applications
Sudipta Chatterjee
GEMTEX – ENSAIT, France

Session B-VII (Salle des Actes)
Chairman: Raz Jelinek

KN B12 17:00–17:25

Molecularly Imprinted Polymers: Biomimetic Synthetic Antibodies

Karsten Haupt
Université de Technologie de Compiègne, France

OR B24 17:25–17:40

Lipase-Catalytic Production of Estolides in Non-Aqueous Media from *Trans*-Hydroxy-Fatty Acids

Àngels Manresa
Universitat de Barcelona, Spain

Session A-VII (Théâtre)

OR A29 17:40–17:55
Biocompatible Silica Nanomaterials Grafted Amphiphilic Block Copolymer and Conjugated with Indocyanine Green
Andrea Schönbächler
University of Applied Sciences and Arts Northwestern Switzerland, Switzerland

OR A30 17:55–18:10
The Influence of Polymers on Growth of Biogenic Crystals in Aqueous Solution and on Solid Surfaces
Helga Fűredi-Milhofer
The Hebrew University of Jerusalem, Israel

OR A31 18:10–18:25
Artificial Biomineral Formed by Incorporation of Copolymer Micelles in Calcite Crystals
Yi-Yeoun Kim
University of Leeds, UK

Session B-VII (Salle des Actes)

OR B25 17:40–17:55
Coherent Synchronized Reactions of Substrates Oxidation by Hydrogen Peroxide
Tofik M. Nagiev
Baku State University, Azerbaijan

OR B26 17:55-18:10
Water-Borne Polyurethane Dispersions Based on Renewable Resources
Yingyuan Li
Eindhoven University of Technology, The Netherlands

OR B27 18:10-18:25
Biosourced Monomers and Resulting (Co)Polymers: towards Original Greener (Co)Polyesters/Polycarbonates/Polyurethanes
Sophie M. Guillaume
Université de Rennes 1, France

18:30-19:00 "Discovering Parc Valrose" (Théâtre)
19:00-22:00 Poster Session & Cheese Party (Salle à manger/Salle des Actes/Salon de Musique)

October 5th (Friday)

Chairman: Vladim V. Tsukruk
PL3 8:30-9:10 Plenary (Théâtre)
Responsive Polymer Hybrid Materials Based on Bio-Inspired Micro- and Nano-Ordered Structures
Bai Yang
Jilin University, P. R. China

Session A-VIII (Théâtre)
Chairman: Bai Yang

KN A11 9:15–9:40 Keynote
Super Water-Repellent Solid Surfaces: Potential Application in Cell Cultures
Hu Yan
Zhengzhou University, P. R. China

KN A12 9:40–10:05 Keynote
A Biomimetic Approach to Enhancing Interfacial Interactions in Polymer Nanocomposites
Xuehong Lu
Nanyang Technological University, Singapore

OR A32 10:05–10:20
Adhesion Studies of Gastrolith Components and Interactions of Modified Cellulose for Biocomposite Formation
Mark W. Rutland
KTH Royal Institute of Technology, Sweden

OR A33 10:20–10:35
Two-Level Hierarchical Superhydrophobicity with Multiple Wetting States
Juuso T. Korhonen
Aalto University, Finland

OR A34 10:35–10:50
Synthesis and Characterization of [Arg-Phe]-Octapeptide Nanostructures Prepared via Solid-Vapor Phase
Emerson R.T. da Silva
Universidade Federal do ABC, Brazil

Session B-VIII (Salle des Actes)
Chairman: Vladim V. Tsukruk

KN B13 9:15–9:40 Keynote
Polydiacetylene – a Unique Chromatic Biomimetic Polymer for Membrane, Bacterial, and Cellular Sensing
Raz Jelinek
Ben Gurion University, Israel

KN B14 9:40–10:05 Keynote
Biomimetic Morphogenesis and Structure of Calcite Statoliths (Otoconia): an Approach towards Deeper Understanding of a Bio-Sensor and its Function
Rüdiger Kniep
Max-Planck-Institute for Chemical Physics of Solids, Germany

OR B28 10:05–10:20
Novel Cellulose Derivatives for Making Modified Porous Cellulosic Materials
Georg Pour
Mines ParisTech, France

OR B29 10:20–10:35
Synthesis and Bone Tissue Reaction of Bone-Like Nanostructured Hydroxyapatite/Collagen Nanocomposites
Masanori Kikuchi
National Institute for Materials Science, Japan

OR B30 10:35–10:50
Selection and Characterization of Diamond-like Carbon Binding Peptides
Bartosz Gabryelczyk
VTT Technical Research Centre of Finland, Finland

Pause 10:50–11:15

Session A-IX (Théâtre)
Chairman: Jim De Yoreo

KN A13 11:15–11:40 Keynote
Nanoparticulate Metal Oxide Matrices for Bio- and Drug Delivery: Synthesis, Function and Bio-Digestion
Vadim G. Kessler
Swedish University of Agricultural Sciences (SLU), Sweden

KN A14 11:40–12:05 Keynote
Structural Proteins: Bio-Inspired Polymers for Fibers, Particles, Films, and More
Thomas Scheibel
Universität Bayreuth, Germany

OR A35 12:05–12:20
High-Performance Ordered Hierarchical Mesoporous Anatase TiO_2 via Biomimetic Synthesis
Jingjie Cui
Hangzhou Dianzi University, P. R. China

OR A36 12:20–12:35
Mesoporous Silica Aerogel – Tricalcium Phosphate – Hydroxyapatite Composite Ceramics for Artificial Bone Substitution
István Lázár
University of Debrecen, Hungary

KN A15 12:35–13:05
Molecular Tectonics: from Molecules to Periodic Architecture
Mir Wais Hosseini

Université de Strasbourg, France

Session B-IX (Salle des Actes)
Chairman: Sam P. de Visser

KN B15 11:15–11:40 Keynote
Poly(ethylene oxide) Based Materials: from Synthesis to Biomedical Applications
Pierre-J. Lutz

Institut Charles Sadron, France

KN B16 11:40–12:05 Keynote
Polymer Brushes: Tuning the Biology-Materials Interface
Christopher K. Ober
Cornell University, USA

OR B31 12:05–12:20
A Bioinspired and All Conducting Polymer for Neural Engineering: a Integrated Platform of Biochemical and Electrical Stimulation
Bo Zhu
RIKEN Advanced Science Institute, Japan

OR B32 12:20–12:35
Computer Modelling of Glucose Dehydrogenase-Based Amperometric Biosensor
Evelina Gaidamauskaitė
Vilnius University, Lithuania

OR B33 12:35–12:50
Adhesion Behavior of Cells on Cerium Oxide Nanoparticle Layers with Stable Trivalent Ions
Tamaki Naganuma
International Center for Materials Nanoarchitectonics, Japan

OR B34 12:50–13:05
Peptide Nanostructures Functionalized with Hypericin
Márcia I. Souza
Universidade Federal do ABC, Brazil

Lunch 13:05–14:35

Session A-X (Théâtre)
Chairman: Jas Pal Badyal

KN A16 14:35–15:00 Keynote
Biotemplating of Optical and Photonic Materials

Cordt Zollfrank
Technische Universität München, Germany

Session B-X (Salle des Actes)
Chairman: Yves Queneau

KN B17 14:35–15:00 Keynote
Bio-Inspired Catalytic Radical-Type Transformations
Bas de Bruin
University of Amsterdam, The Netherlands

Session A-X (Théâtre)

OR A37 15:00–15:15

Geomimetic Chrysotile Inorganic Nanotubes for Technological Applications

Filippo Pierini
Bologna University, Italy

OR A38 15:15–15:30
Fabrication of Asymmetric Microstructures and the Investigation of its Anisotropic Properties
Junhu Zhang

Jilin University, P. R. China

OR A39 15:30–15:45
Photonics with Diatom Nanostructured Silica: an Overview
Edoardo De Tommasi
National Council for Research, Italy

KN A17 15:45–16:10
Structural Color in Plants
Silvia Vignolini
University of Cambridge, UK

KN A18 16:10–16:35
Fabrication and Applications of Polymer Photonic Crystals

Yanlin Song

Chinese Academy of Sciences, P. R. China

Session B-X (Salle des Actes)

OR B35 15:00–15:15
Ring-Opening Polymerization of Heterocycles using Organometallic Complexes: a Simple Access to Biodegradable Polymers
Christophe M. Thomas
Chimie ParisTech, France

OR B36 15:15–15:30
Investigation of Modified Activated Carbon Characteristics by Adsorption Methods
Hoang Kim Bong
Moscow State University of Fine Chemical Technologies, Russia

OR B37 15:30–15:45
Development of High-Performance Poly(lactic acid)s
Hideki Yamane
Kyoto Institute of Technology, Japan

KN B18 15:45–16:10
Bioinspired System for Thermal Energy Management
Tao Deng
Shanghai Jiao Tong University, P. R. China

OR B38 16:10–16:25
CO_2 as Nice Raw Material: Selective Synthesis of Cyclic Carbonates
Lorraine Christ
IRCELYON, France

OR B39 16:25–16:40
Synthesis of Isosorbide Based Polyurethanes: an Isocyanate Free Method
Vincent Besse
Ecole Supérieure de Chimie de Montpellier, France

Pause 16:40–17:05

Session A-XI (Théâtre)
Chairman: Kock-Yee Law

OR A40 17:05–17:20

Biomineralized Carbonates as Binders for Construction Materials

M. Sudhakara Reddy
Thapar University, India

OR A41 17:20–17:35
Properties of Electrospinning-Prepared Poly(ε-Caprolactone)/L-Diphenylalanine Nanocomposites
Michelle S. Liberato
Universidade Federal do ABC, Brazil

Session B-XI (Salle des Actes)
Chairman: Tao Deng

OR B40 17:05–17:20
Aerocellulose: an Ultra-Light and Porous Cellulose. Influence of Processing Parameters on Fine Morphology
Cyrielle Rudaz
Mines ParisTech, France

OR B41 17:20–17:35
Micro-Manufacturing Cellulose Whiskers / Maleic Anhydride Engineered Surfaces with Plasma Polymerization
Michel Brioude
Freiburg University, Germany

Session A-XI (Théâtre)

OR A42 17:35–17:50
Superhydrophobic/Superoleophobic Surfaces Based on Conducting Polymers
Thierry Darmanin
Nice-Sophia Antipolis University, France

Session B-XI (Salle des Actes)

OR B42 17:35–17:50
New Environmentally Friendly Method to Efficiently Extract Cellulose Nanowhiskers
Jia Mao
Freiburg University, Germany

OR B43 17:50–18:05
Study of Interactions between Octyl-b-D-glucopyranoside and the Biopolymer Hydroxyethylcellulose in Drug Delivery
Ximena Villegas-Pañeda
Universidad Nacional Autónoma de México, Mexico

18:10 - Closing Ceremony (Théâtre)

Poster session

POSTER SESSION

P01	Lala Setti Belaroui	University of Oran	
P02	Farid Benkaci-Ali	University of Sciences and Technologies Houari Boumediène	
P03	Makhlouf Boufatit (1)	University of Sciences and Technologies Houari Boumediène	
P04	Makhlouf Boufatit (2)	University of Sciences and Technologies Houari Boumediène	
P05	Fernanda Hoelscher	Universidade Federal do Pampa	
P06	Caroline Laugel	Agro Industrie Recherches et Développements	
P07	Catherine Pinel	IRCELYON	
P08	Antonio Ricci	University of Bari	
P09	Emmanuel Rocca	Université de Lorraine	
P10	Nayana Simon de Vargas	Universidade Federal do Pampa	
P11	Valérie Langlois	Université Paris Est	
P12	Cédric Loubat	Specific Polymers	
P13	Tomasz Baran	Jagiellonian University	
P14	Sultana Boutamine	University of Sciences and Technologies Houari Boumediène	
P15	Dana Georgiana Crivoi	"Rovira i Virgili" University	
P16	Zakia Hank	University of Sciences and Technologies Houari Boumediène	
P17	Bernard Juskowiak	Adam Mickiewicz University	
P18	Davud Karimian	Isfahan University	
P19	Tofik M. Nagiev	Academy of Sciences of Azerbaijan	
P20	Matthieu Sonnati	Nice-Sophia Antipolis University	
P21	Gennifer Padoan	Maflon	
P22	Jeanne Tarrade	Nice-Sophia Antipolis University	
P23	Mélanie Wolfs	Nice-Sophia Antipolis University	
P24	Arnaud Zenerino	Nice-Sophia Antipolis University	
P25	Chahinez Benbayer	Nice-Sophia Antipolis University	

P26	Catarina Esteves	Eindhoven University of Technology	
P27	Alexander Salamianski	Institute of Chemistry of New Materials of NAS of Belarus	
P28	Linlin Xiao	Ruprecht-Karls-University Heidelberg	
P29	Shu Yang	University of Pennsylvania	
P30	Nicolas Helfricht	University of Bayreuth	
P31	Helga F.Bereczki	University of Debrecen	
P32	Hicham Farid	Ecole Nationale Supérieure d'Électricité et de Mécanique ENSEM	
P33	Subhadra Garai	CSIR-National Metallurgical Laboratory	
P34	Mariana Pereda	National University of Mar del Plata	
P35	Dong Xie	Indiana University-Purdue University at Indianapolis	
P36	Rondes Ferreira da Silva	Universidade Federal do ABC	
P37	Sergio Kogikoski Jr.	Universidade Federal do ABC	
P38	Baeckkyoung Sung	Centre de Recherche Paul Pascal	
P39	Marine Blondeau	Université Pierre et Marie Curie	
P40	Zhaocong Chen	Nanjing University	
P41	Corinne Chevallard	CEA-Saclay	
P42	Bora Mavis	Hacettepe University	
P43	Andrónico Neira-Carrillo	Universidad de Chile	
P44	Filippo Pierini	Alma Mater Studiorum Bologna University	
P45	Margarita Chembeleeva	Russian Academy of Sciences	
P46	Elena Doblhofer	Universität Bayreuth	
P47	Sabin Issa	MCMC-ICMPE-CNRS	
P48	Herman Sander Mansur	Federal University of Minas Gerais	
P49	Tihomir Solomun	Federal Institute for Materials Research and Testing	
P50	Maha Ayat	Unité de Développement et de la Technologie du Silicium UDTS	
P51	Chouaib Chettah	University of Mentouri	

P52	Roberta Costa Bianchi	Universidade Federal do ABC	
P53	Myline Cottance	ESIEE	
P54	Eduardo De Tommasi	Institute for Microelectronics and Microsystems, Unit of Naples	
P55	Maria Del Pilar Taboada Sotomayor	State University of São Paulo	
P56	Min Sik Eom	Chung-Ang University	
P57	Lida Fotouhi	Alzahra University	
P58	Masoumeh Hasani	Bu-Ali Sina University	
P59	Akio Kuroda	Hiroshima University	
P60	Marcos Vinicius Foguel (1)	UNESP-Univ Estadual Paulista	
P61	Marcos Vinicius Foguel (2)	UNESP-Univ Estadual Paulista	
P62	Cheng Li	Max Planck Institute for Solid State Research	
P63	Salah Abadli	University Mentouri	
P64	Lamia Bouchama	University of Jijel	
P65	Nawal Boukmouche	University of Jijel	
P66	Yulia Dyakova	Russian Academy of Sciences	
P67	Wen He	Shandong Polytechnic University	
P68	Kahina Lasmi	Unité de Développement et de la Technologie du Silicium UDTS	
P69	Amel Lounas	Unité de Développement et de la Technologie du Silicium UDTS	
P70	Assia Saoudel	University of Jijel	

Plenary Lectures Abstracts

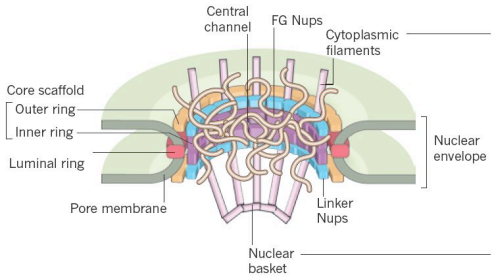
TRANSPORT THOUGH THE NUCLEAR PORE COMPLEX: MECHANISTIC IDEAS AND DEVELOPMENT OF AN ARTIFICIAL NANO-SELECTIVE FILTER

Mirco Sorci,[1] Amit Dutta,[1] Loren Hough,[2] Brian Chait,[3] Mike Rout,[2] Georges Belfort[1,*]

[1]Howard P. Isermann Department of Chemical and Biological Engineering, and Center for Biotechnology and Interdisciplinary Studies, Rensselaer Polytechnic Institute, Troy NY 12180-3590, USA
[2]Laboratory of Cellular and Structural Biology and
[3]Laboratory of Mass Spectrometry and Gaseous Ion Chemistry
Rockefeller University, New York, NY 10065, USA

The Nuclear Pore Complex (NPC) is the sole mediator of exchange between the nucleus and the cytoplasm in all eukaryotic cells. [1] While small molecules pass through the NPCs unchallenged, large macromolecules (>40 kDa) are excluded unless chaperoned across by transport factors collectively termed Karyopherins (Kaps). The translocation of the complexes of Kaps and their cargo proteins/RNAs occurs through the specific affinity and binding between Kaps and particular nuclear pore complex proteins (nucleoporins) called FG-Nups, that share a degenerate multiple-repeated "Phe-Gly" motif. A common aspect of various models explaining the molecular mechanism of selective nuclear transport is that the FG-nups located in the central channel of the NPC form a dense and dynamic network of filaments that blocks translocation of inert molecules, and that this barrier is overcome with the help of Kaps. In an attempt to understand this transport and selective process under crowding conditions, we have conducted single molecule force spectroscopy using volume force mapping with an atomic force microscope. In the spirit of the theme of this conference, we will summarize the various models explaining the molecular mechanism of selective nuclear transport,[1] present our recent findings that relate to the mechanism of transport and selectivity, and demonstrate the testing of an artificial nano-selective filter that mimics the transport selectivity of the nuclear pore complex. [2] Finally, we offer several possible options for further development of a synthetic analog of the NPC.

FIG. 1 CARTOON OF THE BASIC STRUCTURE OF THE NUCLEAR PORE COMPLEX (AFTER REF 1)



[1] D. Grünwald, R.H. Singer, M. Rout, *Nature* **2011**, 475, 333-341.
[2] T. Jovanovic-Talisman, J. Tetenbaum-Novatt, A.S. McKenney, A. Zilman, R. Peters, M.P. Rout, B.T. Chait, *Nature* **2009**, 457, 1023-1927.

NANOMATERIALS ENGINEERING WITH DIATOMS

Nicolas H. Voelcker,[1]* Dusan Losic,[2] Jim Mitchell[3]

[1]*Mawson Institute, University of South Australia 1, Adelaide, Australia*
[2]*Department of Chemical Engineering, University of Adelaide, Adelaide, Australia*
[3]*School of Biological Sciences, Flinders University, Adelaide, Australia*

The unique morphologies of the biosilica frustules of diatoms have arisen through tens of millions of years of evolutionary selection, and are likely to reflect optimised design and function. Translating these lessons in design into approaches in materials engineering is likely to spur the development of new functional material and more nuanced materials. In order to exploit the tremendous opportunities offered by diatoms for the design and production of novel nanostructured materials, one needs to perform the structural equivalent of data mining to gain a deep understanding of the structure function relationships and adopt design blue prints. In this presentation, we review the progress in the field surrounding this new paradigm in materials engineering and focus on efforts in our laboratory and others to produce new nanomaterials based on diatoms using templating approaches and on shape conservative chemical transformation of diatom silica into other chemistries. We will provide examples of applications of such new materials in chemo- and biosensing, particle sorting, microfluidics and photonics.

[1] D. Losic, J.G. Mitchell, N.H. Voelcker, *Adv. Mater.* **2009**, 21, 2947-2958.
[2] D. Losic, J.G. Mitchell, N.H. Voelcker, *Chem. Commun.,* **2005**, 25, 4905-4907.
[3] D. Losic, G. Triani, P.J. Evans, A. Atanacio, J.G. Mitchell, N.H. Voelcker, *J. Mater. Chem.,* **2006**, 16, 4029-4034.
[4] D. Losic, J.G. Mitchell, N.H. Voelcker, *New J. Chem.,* **2006**, 6, 908-914.
[5] D. Losic, G. Rosengarten, J.G. Mitchell, N.H. Voelcker, *J. Nanosci. Nanotechnol.,* **2006**, 6, 1-8.
[6] D. Losic, K. Short, J.G. Mitchell, R. Lal, N.H. Voelcker, *Langmuir,* **2007**, 23, 5014-5021.
[7] D. Losic, J.G. Mitchell, R. Lal, N.H. Voelcker, *Adv. Funct. Mater.,* **2007**, 17, 2439-2446.
[8] D. Losic, R.J. Pillar, T. Dilger, J.G. Mitchell, N.H. Voelcker, *J. Porous Mater.,* **2007**, 14, 61-69.
[9] D. Losic, J.G. Mitchell, N.H. Voelcker, *Proceedings of SPIE,* **2008**, 7267, 726712-1-8.

RESPONSIVE POLYMER HYBRID MATERIALS BASED ON BIO-INSPIRED MICRO- AND NANO-ORDERED STRUCTURES

Yunfeng Li, Zhanhua Wang, Junhu Zhang, Bai Yang*

State Key Lab of Supermolecular Structutre and Materials, College of Chemistry Jilin University, 2699# Qianjin Ave, Chanchun 130012, China

Stimuli-responsive polymer based materials have attracted immense interest in many fields, including smart surface or channels, microfluidic devices, biointerfaces, diagnostics, and sensors. In this abstract, we report 1D and 2D ordered stimuli-responsive polymer hybrid materials by simple techniques. We prepared 1D photonic crystal by alternatively spin-coating responsive polymers and TiO2 gels. Because of the stimuli-responsive of the polymer, the optical properties of the photonic crystal can be changed and controled. As a result, such bybrid photonic crystal can be used as sensors to detect water vapor, solvents, and SCN-. In addation, the 2D hybrid nanopost arrys are prepared by combining colloidal lithography with surface-initiated atom-transfer radical polymerization. Such hybrid nanopost arrys can also be used as sensors. Moreover, the responsive polymer nanoarrys are prepared by colloidal lithography and surface-initiated atom-transfer radical polymerization. The kind of the polymers and feature sizes of the nanoarrys can be arbitrarily tuned by changing the experimental conditions. After conjugating proteins on the polymer arrys, the protein patterns can be obtained. The protein and polymer hybrid anoarrys are promising for biosensors or fundamental biological research.

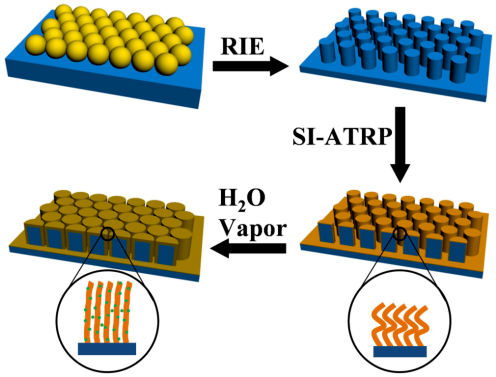


Fig. 1: The fabrication of silicon/polymer composite nanopost arrays and their sensing applications

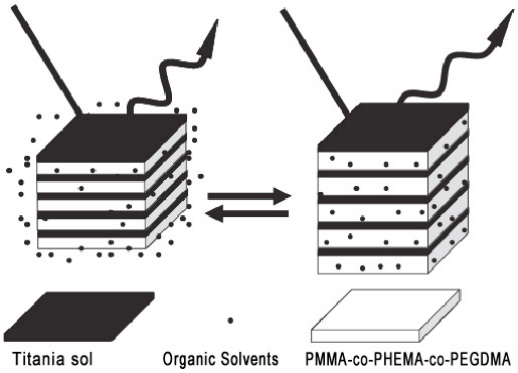


Fig. 2: Colorful detection of organic solvents based on responsive organic/ inorganic hybrid 1D photonic crystals

[1] Y.F. Li, J. H. Zhang, B. Yang, et al., *Small*, **2011**, 7 (19) 2769–2774.
[2] Z. H. Wang, J. H. Zhang, B. Yang. et. al, *Adv. Funct. Mater.*, **2010**, 20, 3784–3790.
[3] Z. H. Wang, J. H. Zhang, B. Yang. et. al, *J. Mater. Chem.*, **2011**, 21,1264–1270.
[4] Z. H. Wang, J. H. Zhang, B. Yang. et. al, *Chem. Commun.*, **2010**, 46, 8636–8638.
[5] Y. F. Li, J. H. Zhang, B Yang et al., *Adv. Mater.*, **2009**, 21 4731-4734.
Acknowledgements: This work was supported by NSFC 91123031

Keynotes Abstracts Session A

BIO-INSPIRED, SMART, MULTISCALE INTERFACIAL MATERIALS

Lei Jiang*

Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Bio-inspired smart materials should be a “live” material with various functions like organism in Nature, they must have three essential elements as sense, drive and control. The studies on lotus and rice leaves reveal that a super-hydrophobic surface with both a large CA and small sliding angle needs the cooperation of micro- and nanostructures. Considering the arrangement of the micro- and nanostructures, the surface structures of the water-strider’s legs were studied in detail. Accordingly, super-hydrophobic surfaces of aligned carbon nanotube films, aligned polymer nanofibers and differently patterned aligned carbon nanotube films have been fabricated. Many methods had been applied in making superhydrophobic films with multi-functional properties, such as structural colored, transparent and/or conductive superhydrophobic films. Under certain circumstances, a surface wettability can switch between superhydrophilicity and superhydrophobicity, just like in Chinese ancient Taiji philosophy that “Yin” and “Yang”, the two opposing fundamental properties of nature, are switchable. The cooperation between surface micro- and nanostructures and surface modification of poly (N-isopropylacrylamide) gave reversible switching. By grafting the copolymer of temperature-sensitive and pH-sensitive components, a dual-responsive surface can be controlled by either or both of temperature and pH was fabricated. Besides organic surfaces, a series of inorganic switchers were also made. UV light stimulated transition between superhydrophobic and superhydrophilic by aligned ZnO, TiO2, and SnO2 films are successfully prepared respectively. Most recently, we developed a superoleophobic and controllable adhesive water/solid interface which opens up a new strategy to control self-cleaning properties in water. To expand the “switching” concept of the smart 2D surface, we also did a lot of interesting work in 1D system. For example, we discovered the water collection ability of capture silk of the cribellate spider Uloborus walckenaerius and then prepared artificial spider silk which will have great applications in water collection. In addition, we developed the novel biomimetic ion channel systems with a variety of intelligent properties (pH responsive, temperature responsive, potassium responsive, zinc activated, and dual-responsive single nanochannels), which were controlled by our designed biomolecules or smart polymers responding to the single external stimulus, provided an artificial counterpart of switchable protein-made nanochannels (highlight by Nature, and Nature China). These intelligent nanochannels could be used in energy-conversion system, such as photoelectric conversion system inspired by rhodopsin from retina or bR, and concentration-gradient-driven nanofluidic power source that mimic the function of the electric eels.

[1] X. Hou, W. Guo, L. Jiang, *Chem. Soc. Rev.*, **2011**, 40, 2385-2401.
[2] Y.M. Zheng, H. Bai, Z.B. Huang, X.L. Tian, F.Q. Nie, Y. Zhao, J. Zhai, L. Jiang, *Nature*, **2010**, 463, 640-643.
[3] M.J. Liu, Y.M. Zheng, J. Zhai, L. Jiang, *Acc. Chem. Res.*, **2010,** 43, 368-377.
[4] L.P. Wen, X. Hou, Y. Tian, F.-Q. Nie, Y.L. Song, J. Zhai, L. Jiang, *Adv. Mater.*, **2010**, 22, 1021–1024.
[5] W. Guo, L. X. Cao, J. C. Xia, F. Q. Nie, W. Ma, J. M. Xue, Y. L. Song, D. B. Zhu, Y. G. Wang, L. Jiang, *Adv. Funct. Mater.*, **2010**, 20, 1339-1344.
[6] F. Xia, L. Jiang, *Adv. Mater.*, **2008**, 20, 2842-2858.
[7] X.J. Feng, L. Jiang, *Adv. Mater.*, **2006**, 18, 3063-3078.
[8] S.T. Sun, L. Feng, X.F. Gao, L. Jiang, *Acc. Chem. Res.*, **2005**, 38, 644-652.
[9] X.F. Gao, L. Jiang, *Nature*, **2004**, 432, 36.
[10] L. Feng, S.H. Li, Y.S. Li, H.J. Li, L.J. Zhang, J. Zhai, Y.L. Song, B.Q. Liu, L. Jiang, D.B. Zhu, *Adv. Mater.*, **2002**, 14(24), 1857-1860.

SURFACE-ADHESIVE AND BIOACTIVE SELF-ASSEMBLED PEPTIDE NANOFIBERS FOR BIOINSPIRED FUNCTIONALIZATION OF METAL SURFACES

Mustafa O. Guler,* Ayse B. Tekinay, Hakan Ceylan, Samet Kocabey

Bilkent University, Institute of Materials Science and Nanotechnology, National Nanotechnology Research Center (UNAM), Ankara, Turkey 06800

Integration of metal-based implants into the existing tissue is a major problem. Herein, we demonstrate biofunctionalization of metal surfaces through mussel-inspired adhesion mechanism conjugated to self-assembled peptide nanofibers in order to overcome biocompatibility issues. Dopa conjugated peptide nanofiber coating was used along with bioactive peptide sequences for specific cell-materials interactions on metal surfaces. Dopa-mediated immobilization of bioactive peptide nanofibers on metal surfaces created a bio-specific interface between cells and the metal substrate. This biofunctionalization strategy can be extended into various surface immobilization systems owing to the versatile adhesive properties of Dopa and the ease of ligand conjugation to peptide amphiphile molecules.

[1] H. Ceylan, A.B. Tekinay, M.O. Guler, *Biomaterials*, **2011**, 32, 8797.
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BIOMIMETIC NANOCOMPOSITES BY SELF-ASSEMBLY

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Biological materials can have a synergistic combination of stiffness, strength, toughness, and low density due to aligned self-assemblies between hard reinforcing and soft energy dissipating self-assembled domains. Classic examples are provided by pearl of nacre and silk. A challenge in materials science is to mimic the essential features of them in scalable ways to allow technologically relevant materials. Previously it has been observed that hierarchical self-assemblies can be achieved by combining tectons of different sizes using supramolecular principles (1). Here we address biomimetic nanocomposites based on hierarchical assembly based on colloidal level platelets and nanofibers (larger units) and polymers (smaller units) and their molecularly tailored supramolecular interactions (2-8). An essential aspect is to design energy dissipation and dynamics in the confined soft polymer layers. We show routes for stiff and strong materials and routes towards toughness by tailored nanomechanics.

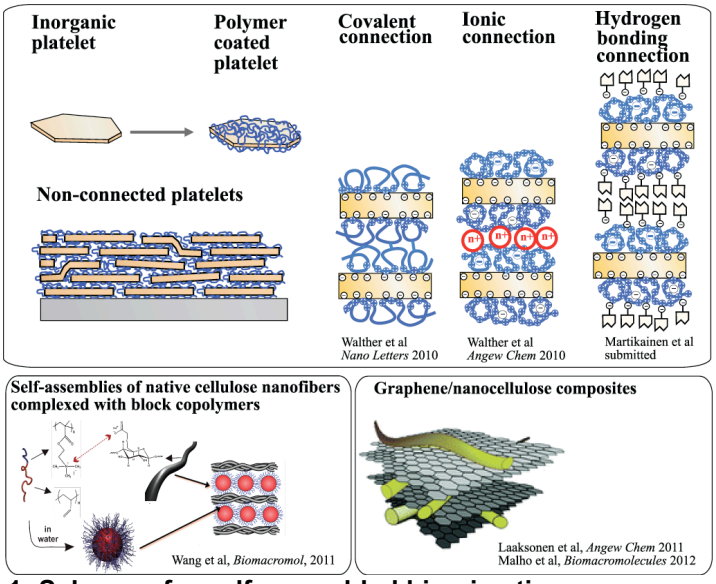

Fig. 1: Schemes for self-assembled biomimetic nanocomposites

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ON THE VERSATILITY OF SILK FIBROIN AS A DESIGNER POLYMER

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As one of the most commonly encountered biomacromolecules, silk affords unique material properties, as exemplified by the tenacity of the fibers comprising cobwebs. In this work, we explore some of the interesting uses of silk fibroin (SF), extracted from *Bombyx mori* silk. Novel protein blends have been prepared by mixing gelatin (G) with SF and using aqueous methanol (MeOH) to post-induce SF crystallization. When co-cast from solution, amorphous blends of these polymers appear homogeneous, as discerned from visual observation, microscopy and Fourier-transform infrared (FTIR) spectroscopy. Upon subsequent exposure to aqueous MeOH, SF undergoes a conformational change from random coil to β sheet. This transformation occurs in pure SF, as well as in each of the G/SF blends, according to x-ray diffractometry and thermal calorimetry. The influence of MeOH-induced SF crystallization on structure and property development has been ascertained in terms of preparation history and blend composition. Thermal gravimetric analysis reveals that the presence of β sheets in SF and G/SF blends improves thermal stability, while extensional rheometry confirms that SF crystallization enhances the tensile properties of the blends. By preserving a support scaffold above the G helix-to-coil transition temperature, the formation of crystalline SF networks in G/SF blends can be used to stabilize G-based hydrogels for biomaterial and pharmaceutical purposes. The present study not only examines the properties of G/SF blends before and after SF crystallization, but also establishes the foundation for future research into thermally-responsive G/SF bioconjugates. Complementary dynamic rheological measurements reveal solid-liquid cross-over at the G helix-coil transition temperature typically between 30 and 36 °C in blends prior to the formation of b-sheet crystals. Introducing the b-sheet conformation in SF stabilizes the hydrogel network and extends the solid-like behavior of the hydrogels to elevated temperatures beyond body temperature with as little as 10 wt% SF. The temperature-dependent elastic modulus across the G helix-coil transition is reversible, indicating that the conformational change in G can be used in stabilized G/SF hydrogels to induce thermally triggered encapsulant release. In addition to these protein blends, we demonstrate that SF can be used in conjunction with synthetic polymers and ionic liquids to generate novel materials with interesting properties that will greatly extend the versatility of SF as a designer polymer.

SUPER-HYDROPHOBICITY AND SUPER-HYGROPHOBICITY: IN AIR, UNDER A LIQUID, ON A LIQUID

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Many plants and insects use super-hydrophobicity as one of their survival mechanisms. The fundamental principles underlying super-hydrophobicity are presented and discussed for a water drop on a solid surface in air, for a surface under water, and for a surface floating on water. Recent fundamental contributions regarding the feasibility of such states are described. Special emphasis is put on the possible metastability of the super-hydrophobic state, which is apparently used in Nature as a compromise in order to get better super-hydrophobicity at a lower "cost". In addition, super-hygrophobicity (non-wettability by liquids in general) is discussed.

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FUNCTIONAL NANOCOATINGS FOR SURFACE BIOMIMETICS

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A major element of research undertaken in the field of surface biomimetics has focused on the replication of naturally occurring systems. Well known examples being plant leaves (in particular the *Nelumbo nucifera* (Lotus) leaf), insect wings, bird feathers, water strider legs, and biofilms. Many of these possess surface structures consisting of micro- and nanoscale features, together with an inherent surface chemistry. A variety of approaches (e.g. photon and electron beam lithography, reactive ion etching, and micromachining) have been developed to replicate these structures on substrate surfaces akin to those observed in nature. However in such cases, appropriate surface chemistry has to be subsequently introduced as a separate step in order to achieve the overall sought biomimetic behaviour. A novel approach will be described where both replication and surface functionalisation can be combined into a single step to create multiple functionalised replica surfaces. This will be illustrated using natural templates such as plants, insects, and marine species for technological applications such as superhydrophobicity, fog harvesting, and adhesion.

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SANDCASTLE WORMS AND CADDISFLY LARVA: INSPIRING NEW BIOMATERIALS THROUGH CO-POLYELECTROLYTE CONDENSATION

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The sandcastle worm, a marine polycheate, cobbles together composite tubular dwellings with sand, the broken exoskeletons of marine invertebrates, and undersea glue. The tubes are adjoined to other tubes to create intertidal reefs reminiscent of sandcastles, hence the common name. Caddisfly larvae, freshwater insects, assemble composite structures remarkably similar to sandcastle worm tubes in look and function using a sticky underwater silk (fig.1). The adhesives are chemically similar in that they both comprise oppositely charged polyelectrolytes. Further, the sandcastle glue and caddisfly silk both contain high molar ratios of acidic phosphoserines (pSer), 26 mol% and 10 mol%, respectively, balanced by high molar ratios of basic residues. [1,2] The oppositely charged residues of the sandcastle worm glue are distributed in different proteins, whereas the oppositely charged residues of the caddisfly silk are distributed as alternating blocks in the polyampholytic heavy chain fibroin protein, the major component of the silk. Both adhesives contain divalent cations (Ca^{2+} and/or Mg^{2+}). The sandcastle glue is secreted as dabs of a colloidal solution, whereas the caddisfly silk is drawn from labial spinnerets as a nano-structured adhesive tape (fig.1). Together, these examples suggest intermolecular charge neutralization between oppositely charged regions of polyelectrolytic biomacromolecules, with consequent expulsion of small counter ions and water as an entropic driving force, may be a common mechanism in nature to create insoluble underwater adhesives from water-soluble macro-precursors. Accordingly, the sandcastle worm and caddisfly adhesives provide a new paradigm for the design of biomimetic medical adhesives based on polyelectrolyte condensation. The chemistry, material form, and function have been copied with pairs of oppositely charged copolyelectrolyte analogs that mimic the chemistry (phosphates and amines) and molar ratios of the electrolytic sidechains of the natural sandcastle glue proteins.[3] When the synthetic analogs are mixed under the right conditions they condense into a phase-separated fluid of concentrated polymers—a complex coacervate—that has ideal properties as the foundation for water-borne, wet environment adhesives. Because complex coacervates are phase separated from water they can be applied underwater without dissolving, and after setting they do not absorb water and swell. Yet, they have a miniscule interfacial tension with water that allows them to readily spread on wet surfaces. They are denser than water (and blood) so they don't float, the electrolytic sidechains displace surface bound water and ions to promote interfacial adhesion, and the viscosity decreases dramatically under shear, aiding flow and injectability. Solid phases can be incorporated to increase bond strength. Water-soluble components can be incorporated to increase functionality. Because the sandcastle glue was naturally adapted for joining wet biogenic minerals, one of the first clinical targets has been mineralized tissue repair. [4] Soft tissue adhesives are also being developed.

Fig 1. A.) Sandcastle worm. B.) SEM of 0.5 mm beads bonded with sandcastle glue. C.) Caddifly larva. D.) SEM of 0.5mm beads taped together with sticky silk.

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PATHWAYS OF MATRIX PROTEIN SELF-ASSEMBLY AND SUBSEQUENT MINERAL NUCLEATION

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Self-assembly of organic matrices and subsequent directed nucleation of the mineral constituents is a widespread paradigm in biomineral formation. The architecture of the underlying matrix imposes order on the nucleating mineral species. For example, in bone collagen monomers form into triple helices, which then self assemble into well-organized fibrils. Within these fibrils highly-oriented hydroxyapatite crystals nucleate and grow with a specific crystal face in contact with the collagen fibrils. In order to understand the underlying physical controls governing both matrix self-assembly and biomolecule-directed crystallization, we are using *in situ* AFM and TEM combined with single molecule dynamic force spectroscopy (DFS) molecular dynamics (MD) to investigate these processes.

In situ AFM investigations into the assembly of extended protein structures formed from both collagen and microbial S-layer membrane proteins reveal the key role of conformational transformations in controlling the pathways and kinetics of matrix assembly. The large barriers associated with these transformation renders them rate-limiting in forming the ordered structures. Consequently, before the ordered state can emerge, these systems must be driven to condense into metastable, liquid-like clusters in which protein-protein contact times are large. The emergence of order within these clusters catalyzes the further transformation and attachment of the monomeric proteins. In addition, DFS measurements show that subtle changes in the binding free energy both between the proteins and with the substrates can drive the system to adopt radically different architectures. Moreover, the pathway to the final ordered state can pass through transient, less-ordered conformational states. Thus the concept of a folding funnel with kinetic traps often used to describe folding of individual proteins is also applicable to protein matrix self-assembly.

In situ AFM and TEM studies of mineral nucleation dynamics on organic monolayers and collagen matrices show that these surfaces promote nucleation through a reduction in the interfacial energy. However, nucleation of the amorphous phase in the calcium phosphate-on-collagen system is observed at supersaturations that are too low to be explained by classical nucleation theory (CNT). The existence of pre-nucleation clusters is shown to provide a low-barrier pathway to crystallization that circumvents the large barriers predicted by CNT. Molecular dynamics simulations of clustering in solutions that utilize replica exchange methods to reach large cluster sizes with accurate potentials reveals the common occurrence of multi-ion clusters and $CaCO_3$ formation of 3D polyhedra that can be mapped to the hydrated crystal structures. Efforts are currently underway to compute the free energy landscape of the clusters in order to develop a predictive understanding of cluster-driven nucleation on organic matrices.

Finally, in order to understand these cluster- and particle-mediated crystallization processes, we have performed *in situ* high-resolution TEM using a custom-built fluid cell. We show that primary nuclei undergo continuous rotation and interaction until they find a perfect lattice match. A sudden “jump to contact” then occurs over < 1nm, followed by lateral atom-by-atom addition initiated at the contact point. Interface elimination proceeds at a rate consistent with the curvature-dependence of the Gibbs free energy. Measured translational and rotational accelerations show that strong, highly-direction-specific interactions drive crystal growth via oriented attachment of primary nuclei.

Taken together, these results provide new insights into the physical mechanisms controlling biological and biomimetic crystallization, from the formation of the initial protein matrix to the maturation of final crystalline structures.

DESIGN, SURFACE PROPERTIES AND APPLICATIONS OF ROBUST SUPEROLEOPHOBIC SURFACES

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Digital office color printers and offset color presses are basically complex electromechanical devices that put images of toner and ink on paper. Contamination of the print surface by toner and ink has been a key failure, hindering high speed, high quality printing. Inspired by the self cleaning effect of the Lotus leaves, we have launched a systematic investigation to explore if print surfaces with micro/nanostructures can enable easy-clean, self-clean and offset free feature in future printing engines. Since all the toner and ink materials are organic, our attention has been on surface with superoleophobic properties. Earlier, we [1] report the fabrication of a model superoleophobic surface comprising ~3 μm diameter pillar arrays (6 μm pitch with height at 7.8 μm) on silicon wafer via the conventional photolithography and surface fluorosilanation techniques. Results showed that both surface fluorination and the re-entrant structure in the side wall of the pillar are crucial in achieving the Cassie-Baxter state that leads to superoleophobicity as well as superhydrophobicity with hexadecane and water contact angles at >150° and sliding angles at ~10°. Further studies have been conducted to understand the effects of pillar height, size and spacing not only on the superoleophobicity, but also on the robustness of the surface against wetting and mechanical abrasion under external pressure. Results showed that while both static and advancing contact angles remain "super" (>150°) as the pillar size and the pillar spacing vary, the receding contact angle, sliding angle and contact angle hysteresis are found to be sensitive to these structural changes. The receding angle decreases and both sliding angle and hysteresis increase as the solid area fraction increases. On the other hand, surface superoleophobicity & superhydrophobicity remain unchanged as the height of the pillar decreases from 7.8 to ~1 μm. Surface Evolver simulation was used to model the location of the three phase contact line as well as the robustness in wetting against external pressure. The abrasion resistance of the pillar array surface was assessed via mechanical modeling and nanoindenter measurement. The design space for fabricating superoleophobic/superhydrophobic surface that is robust against both wetting and mechanical abrasion under pressure is discussed. As for technology application, the potential uses of the surfaces in self cleaning printhead and off-set free fusing will be discussed.

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BIO-NANOCOMPOSITES BASED ON CELLULOSE NANOFIBERS (FROM AGRICULTURAL BIOMASS) REINFORCED IN THERMOPLASTIC STARCH POLYMER

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Keywords: green nanocomposites, cellulose nanofibers, TEM, DMA, TGA.

This research work focus on the green nanocomposite materials prepared by reinforcing cellulose nanofibers in Thermoplastic starch (TPS) as biopolymer matrix. The cellulose nanofibers were isolated from wheat straw fibers by chemical and high shear mechanical treatment. These nanofibers were reinforced in thermoplastic starch polymer matrix by using solvent casting method to prepare green nanocomposites. The cellulose nanofibers were characterized by using TEM, SEM, TGA, XRD and FTIR. The TEM images of the wheat straw fibers confirmed their nanostructure and revealed the diameter in the range 30-60nm. Nanocomposite films were characterized by using SEM, XRD, DMA and TGA. The SEM analysis of the films showed the fine fiber adhesion in the polymer matrix. XRD study revealed the improvement in the crystalline nature with the addition of cellulose nanofibers. Dynamic mechanical analysis (DMA) indicated improvement in the mechanical behavior of the fiber reinforced green nanocomposites as compared to neat thermoplastic starch film. There was an increase in residue left with enhancement in cellulose nanofibers percentage as depicted by TGA. Further thermal degradation kinetics of green nanocomposites and neat TPS films were studied by using TGA data obtained at different heating rates. This thermal degradation study revealed enhancement in the activation energy of the nanocomposite films with the addition of nanofibers.

SUPER WATER-REPELLENT SOLID SURFACES: POTENTIAL APPLICATION IN CELL CULTURES

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Solid surfaces in contact with biological cells play an important role in cell cultures. *In vivo*, most cells are embedded within an intricate extracellular matrix, which not only binds the cells and tissues together but also influences cellular development, polarity, and behaviour. Recently, tissue engineering has attracted attention because of the potential of cell transplantation as an alternative therapeutic strategy for tissue repair and organ replacement. Transplanted cells cultured from healthy tissue of a patient can be implanted back into the patient without requiring an immuno-isolation system. In cell cultures for tissue engineering, a matrix scaffold is necessary for adhesion of the cells, requiring a thorough study of potential substrates for the cell culture scaffolds. In this talk I present super water-repellent surfaces (Fig. 1) we studied. [1-2] Preparation and physical properties are presented first followed by highlights of recent progress in cell culture on the solid surfaces. [3-5]

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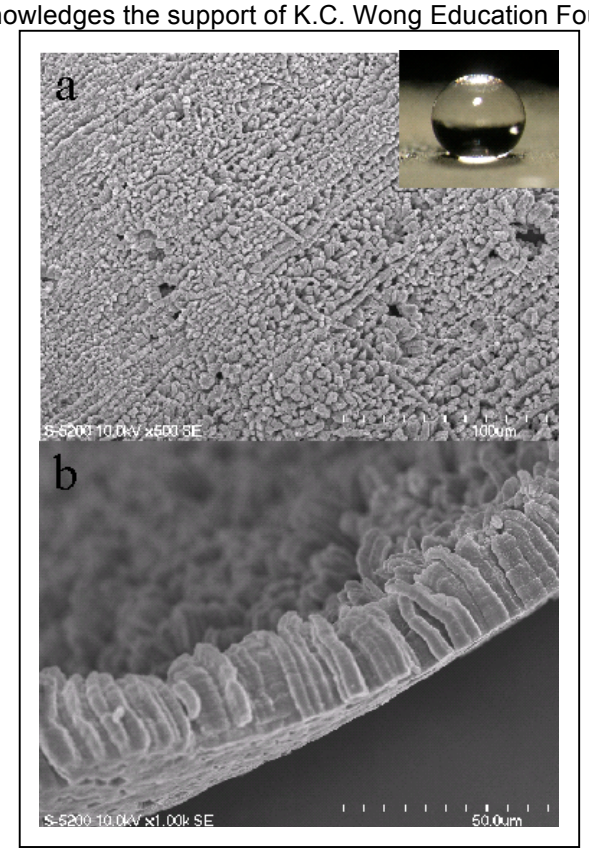

Fig. 1: Super water-repellent poly(alkylpyrrole) film. (a) Top view; (b) side view.

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A BIOMIMETIC APPROACH TO ENHANCING INTERFACIAL INTERACTIONS IN POLYMER NANOCOMPOSITES

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Recently, marine mussel adhesive proteins (MAPs) have attracted great attention owing to the amazing ability of mussels to adhere to various kinds of surfaces. The MAPs contain large amounts of a particular amino acid known as 3,4-dihydroxy-L-phenylalanine (dopamine), which is found at high concentrations at the adhesive interfaces between the mussels and substrates. Previous research work has shown that the catechol groups in dopamine are capable of forming hydrogen bonds, metal-ligand complexes, and quinhydrone charge-transfer complexes, which afford the mussels with strong adhesion to various types of materials. Inspired by these work, we hypothesized that if a thin catechol-rich polymer layer can be prepared as the interface between nanofillers and polymers, the interfacial interactions may be significantly enhanced and hence the thermo-mechanical properties of the nanocomposites can be greatly improved at very low inorganic loadings owing to the more effective stress transfer.

To verify the hypothesis, we prepared dopamine-modified clay (D-clay) and dispersed the D-clay into various types of polymers, including epoxy [1], polyether polyurethane and nylon. This talk will introduce the unique structures, morphologies and thermo-mechanical properties of these novel materials and discuss the structure-property relationships, especially the impact of the impressive interfacial interactions brought by the incorporation of D-clay. Furthermore, the structural evolution of dopamine-modified graphene oxide (DGO) will also be discussed and DGO-based functional composites will be demonstrated [2].

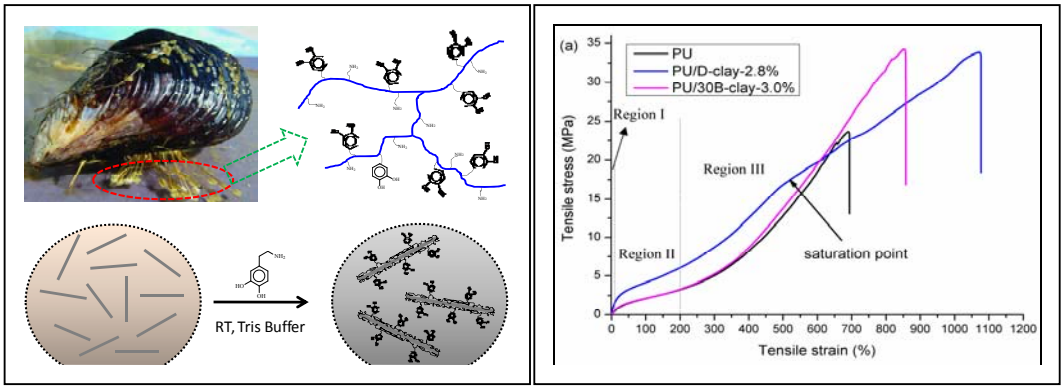

Fig. 1: Modification of clay with dopamine (left) and impressive tensile properties of PU/D-clay

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NANOPARTICULATE METAL OXIDE MATRICES FOR BIO- AND DRUG DELIVERY: SYNTHESIS, FUNCTION AND BIO-DIGESTION

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Inorganic materials receive increasing interest as components and major constituents of encapsulation formulations for bio-molecules and microorganisms. Sol-gel technology is broadly recognized as a versatile synthetic approach to colloidal inorganic materials, perspective as potential hydrosol and hydrogel matrices for encapsulation. The industrial development in this field has been mostly focused on silica in the view of the availability of both organic and inorganic precursors of silica gels and, especially, due to their easy handling and facile control over gelation parameters. Metal oxides have been until recently practically excluded from this application domain, because of the high chemical reactivity and apparent bio-incompatibility of the related precursor chemicals. However, metal oxides with compositions corresponding to naturally abundant biocompatible minerals, for example titanium dioxide (registered even as the Food Additive E171), can represent an attractive alternative to silica. Stable and biocompatible hydrosols and hydrogels of titanium dioxide and other metal oxides can be successfully prepared using modification of the related metal organic precursors with hydrophilic ligands, especially if the latter can be supplied with electric charge through interaction with acids, bases or inorganic anions [1]. The produced colloids are then naturally buffered within biocompatible pH region. An attractive feature of the thus produced colloid particles is that they possess a core-shell structure: the crystalline core contributes with attractive UV-protective properties, while the amorphous shell hinders the negative photochemical activity and permits easy aggregation of the particles into continuous films, self-assembling at any phase boundary, for example, a cell membrane of a microorganism. This permits to produce formulations able to protect the encapsulated biomaterial from both chemical and physical hazards. Another attractive feature of titanium dioxide is its specific biodegradability, offering possibility of enhanced chemically and bio-chemically triggered release [2].

Metal oxide surfaces possess even a pronounced affinity to carboxylate and phosphate/phosphonate functions present in the formula of many important medicines. Release of these drugs after their chemosorption in the oxide hydrogels is a slow and kinetically controlled process sought in many medical applications, which makes the produced materials attractive for drug delivery applications.

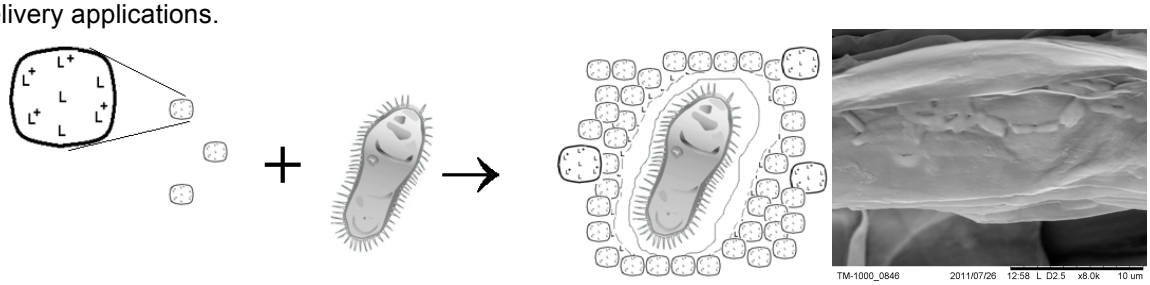

Fig. 1: Bacterial encapsulation in a sol-gel matrix (left) and beneficial bacteria *Bacillus amyloliqufaciens 5113* immobilized on a root of *Arabidopsis taliana* plant (right)

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STRUCTURAL PROTEINS: BIO-INSPIRED POLYMERS FOR FIBERS, PARTICLES, FILMS, AND MORE

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Proteins reflect one fascinating class of natural polymers with huge potential for technical as well as biomedical applications. One well-known example is spider silk, a protein fiber with excellent mechanical properties such as strength and toughness [1, 2]. During 400 million years of evolution spiders became outstanding silk producers. Most spider silks are used for building the web, which reflects an optimized trap for flying prey. Another example of an outstanding protein fiber is mussel byssus [2]. Some marine species like the blue mussel (*Mytilus galloprovencialis*) are able to settle among seabed stones, pales and harbor walls. These mussels have successfully adapted to changes in tides, wind and sun. Their success is based on a unique anchorage, the mussel byssus. Byssus threads show unusual mechanical properties, since they resemble soft rubber at one end and rigid nylon at the other, and these properties are found with a seamless and gradual transition.
We have developed biotechnological methods using bacteria as production hosts which produce structural proteins mimicking the natural ones [3]. Besides the recombinant protein fabrication, we analyzed the natural assembly processes [4, 5] and we have developed spinning techniques to produce protein threads closely resembling natural silk or mussel fibers. Importantly, we can employ the bio-inspired proteins also in other application forms such as hydrogels, particles, non-woven mats, foams or films [6, 7].
Our bio-inspired approach serves as a basis for new materials in a variety of medical, biological, or chemical applications.

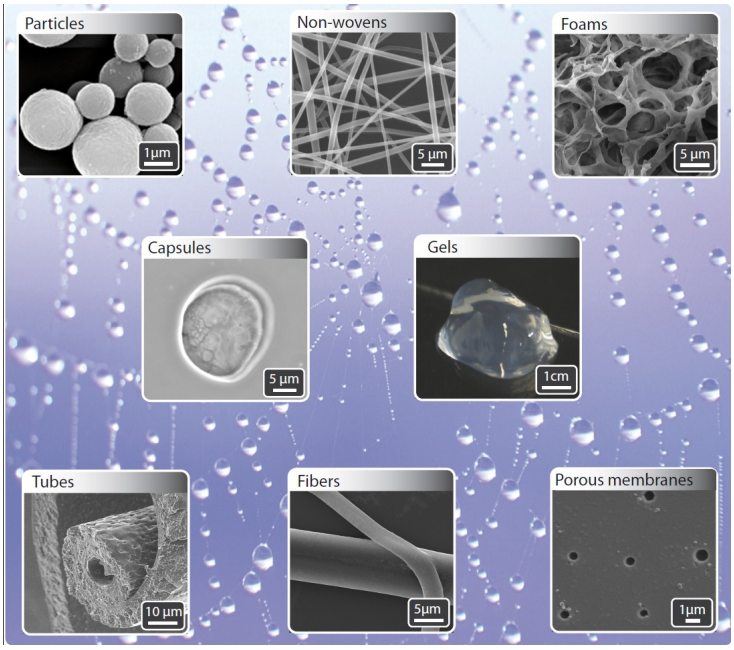

Fig. 1: Assembly forms of a recombinant spider silk protein

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MOLECULAR TECTONICS: FROM MOLECULES TO PERIODIC ARCHITECTURE

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The design and construction of periodic architectures in the crystalline phase or at surfaces are attracting considerable interest over the last two decades. For both design and analysis of molecular crystals, we have developed a strategy called molecular tectonics which is based on the formation of molecular networks through the design of complementary tectons or molecular construction units. The generation of molecular networks and subsequently of crystals is achieved by self-assembly processes based on repetitive molecular recognition events. This approach, combining supramolecular synthesis and self-assembly processes in the solid state, is operational and versatile and allows the design and construction of a variety of complex purely organic or hybrid architectures. The approach will be presented and illustrated by a variety of tectons and networks.

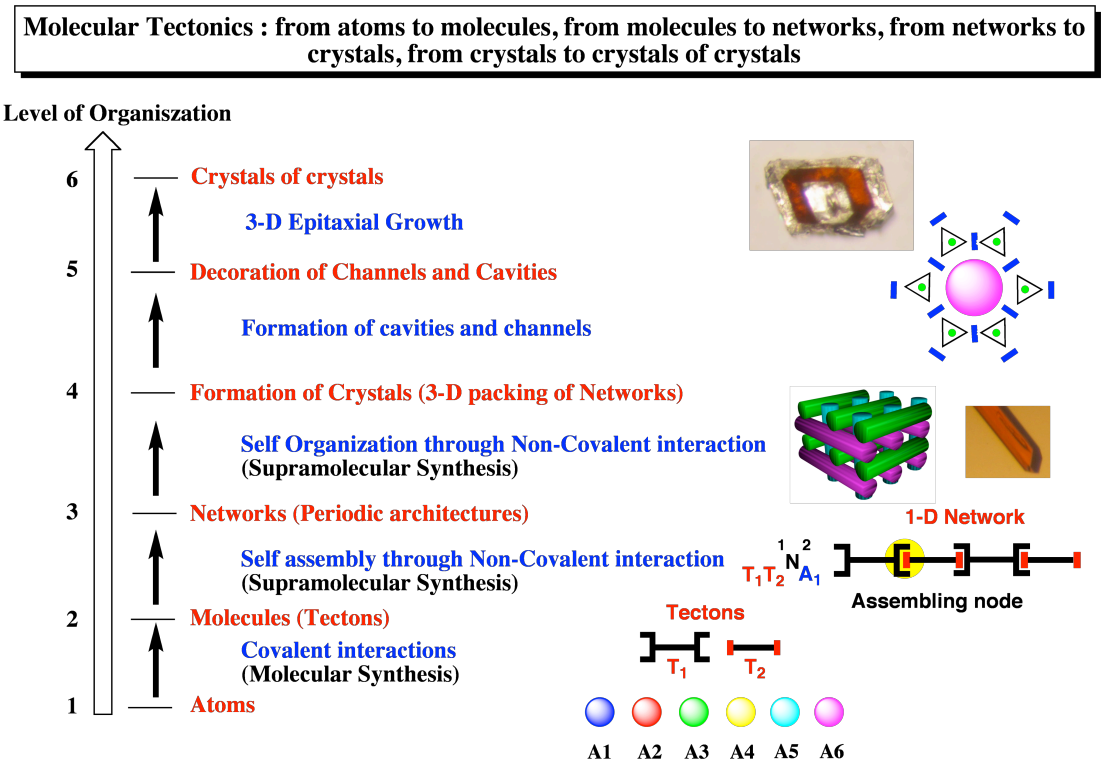

Fig. 1: From atoms to crystals

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BIOTEMPLATING OF OPTICAL AND PHOTONIC MATERIALS

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Microstructured optical and photonic materials and devices have become a matter of increased interest. The multidimensionality of biotemplates with respect to their cellular structures and their inherent anisotropy is beneficial for the development of a bioinspired optical materials design. Biotemplated optical materials are intriguing since they possibly show increased sensitivity, improved spatial resolution and accelerated signal processing in short time domains. The hierarchical cellular tissue anatomy of the three dimensionally structured biotemplate provides the microenvironment to achieve size, shape and orientation control of the inorganic optical material.

Current research on the development of optical and photonic material structure will be presented. Patterned phosphor materials gained increasing interest for high-resolution screen and imaging devices. We show the development of biotemplated Eu^{3+}-doped Y_2O_3 by replication of wood templates. [1] Other phosphor materials exhibiting long lasting phosphorescence or photostimulated luminescence (PSL) are interesting materials for accumulation and storage of photon-derived energy. These materials have potential applications in road markings, electrical power-free illumination, information storage devices and safety labelling applications in case of public light blackouts. Biotemplating of phosphors based on Eu^{2+}-doped $SrAl_2O_4$ and Eu^{2+}-doped BaFBr [2,3] confirmed, that the original wood cell walls are fully transformed into the respective inorganic material while the original anisotropic wood structure was preserved. Patterning of PSL phosphor materials is attractive for high-resolution screen and medical imaging devices.

Photonic materials found in nature can comprise highly complex one- two- or three-dimensional structures that currently cannot be reproduced by artificial structuring techniques. Photonic structures have recently attained strong research interest. Our work shows a route to directly replicate natural photonic D-surface structures into monolithic amorphous inorganic silica, which is capable of withstanding temperatures up to 600 °C. [4] The structures contained in the scales of the beetle *Entimus imperialis* were used for application of our biotemplating approach. Processing involved harvesting the scales, infiltrating them with different polydivinyl- and polyhydromethylsiloxane mixtures and curing the latter in the presence of platinum complexes by hydrosilylation. An adapted heating cycle subsequently removed the organic photonic template and yielded a replica of the original structure. This successfully replicated the natural photonic crystal. We were able to tune the shrinkage from 12% to 40% by varying the siloxane precursor molecule chain length and calcination temperature. Therefore, this rapid, two-step process allows not only to create photonic structures that are high-temperature resistant but are also adapted in their photonic response to the subsequent implementation.

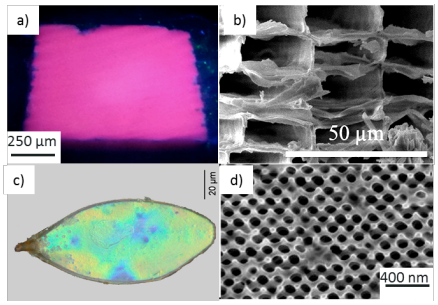

Fig. 1: a,b) Biotemplated Eu^{3+}-doped Y_2O_3, form wood, c) scale of *Entimus imperials* and d) silica replica of the photonic part of the scale.

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STRUCTURAL COLOR IN PLANTS

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Animals use structural color and iridescence for species recognition and mate selection. For similar reasons, many species of plants develops photonic structures: flowers develop grating-like structures to produce iridescent coloration, leaves develop multilayers to protect them from UV-light and fruits create chiral photonic crystal to produce brilliant and attractive coloration.
Structural color in nature is generally associated to animal kingdom and various typologies of photonic crystal structures have been observed in many different insect species like beetles, butterflies, but also in bird feathers and many sea animals[1]. On the counterpart, the structural color in plants is only very rarely reported in the literature. Multilayer structures producing blue coloration have been observed in leaves[2] and in some tropical fruits[3,4]. Recently it has been observed that structural color is, however, quite well spread also in the plat kingdom especially in flowers[4-6].
In this work several mechanisms of structural color in flowers and fruits and leaves are reviewed. In particular, a complete optical and morphological characterization of iridescence in flowers is presented. A waxy diffraction grating in the petal's epidermis superposed on the dark pigment-based coloration provides a unique optical effect that improves the visibility of the flower for pollinators. In the case of fruits and leaves more complicated optical mechanisms are found. In particular, sophisticated cellulose-based chiral multilayer produces an intense and bright blue coloration that gives rise to one of the largest reflectivity observed in nature. Such biological photonic structures, optimized through millennia by the rigorous competition of evolution, can provide broad inspiration for novel artificial and multifunctional photonic materials.

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FABRICATION AND APPLICATIONS OF POLYMER PHOTONIC CRYSTALS

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Photonic crystals (PCs) in nature not only have beautiful colours, but also could effectively modify the emission and propagation of light with minimal losses, thus the fabrications and applications of PCs have attracted extensive research interest. In our group, PCs with high strength were prepared from latex spheres with a hard PS core and an elastometric PMMA/PAA shell [1]. The mono-dispersed latex spheres were synthesized via one-step emulsion polymerization without purification [2a]. PC films with brilliant colours covering the wavelength period from the UV to the IR can be fabricated over large areas by vertical deposition method and even spray coating [2b,2c]. The wettability of the PCs could be well controlled from superhydrophilicity to superhydrophobicity by adjusting the assembly temperature or pH [3]. Furthermore, functional polymer inverse opals were achieved by using the PCs as template, such as high stable polyimide inverse opal PCs [4a] and an electrically tunable polypyrrole inverse opal [4b]. Additionally, as the PC stop band is sensitive to its lattice constant and the relative index of its components, the colorful humidity-sensitive PC hydrogel [5a] and oil-sensitive inverse opals [5b, 5c] were achieved. Moreover, the PCs could be used as wavelength-selective concentrator and effectively improve the output power of dye-sensitive solar cells [6]. The PCs could also be utilized in UV protection, colorful coating materials [2a], and to enhance the fluorescence emission [6a] of dyes and energy transfer of plasmonic device [7b]. Furthermore, by using the PCs' superior properties in localizing the emission, the sensitivity of DNA detection system based on fluorescence resonance energy transfer were greatly improved, and an ultrasensitivity detection down to 13.5 femtomolar was achieved [8]. Furthermore, a 40-fold enhancement of fluorescence signal and 7-fold on/off ratio amplification were obtained by introducing PCs into an optical memory system [9].

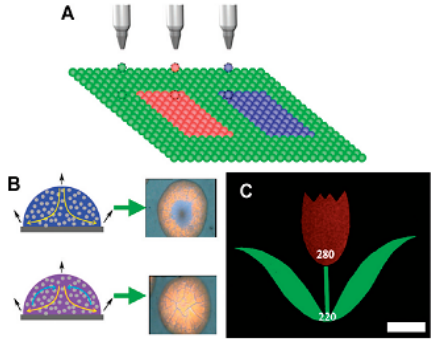

Fig. 1. A photonic crystal pattern prepared by inkjet printing.

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Keynotes Abstracts Session B

A BIOMIMETIC APPROACH TOWARDS NEW PSEUDO GLYCOCONJUGATES FOR SUPRAMOLECULAR APPLICATIONS

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Carboxymethylglycoside lactones (CMGLs) are synthons which allow straightforward access to variously functionalised glycosides (Fig. 1). These bicyclic lactones are obtained by 1,2-ring closure of carboxymethyl glucosides. By reaction of CMGLs with nucleophilic species, notably amines, functional carbohydrate derivatives can be synthesized. After lactone opening, a free hydroxyl group at position 2 is available for a second substitution. The lecture will show the latest developments and provide an overview on the scope of the method [1-5], among which new membrane imaging probes, carbohydrate containing polymers and liquid crystalline derivatives.

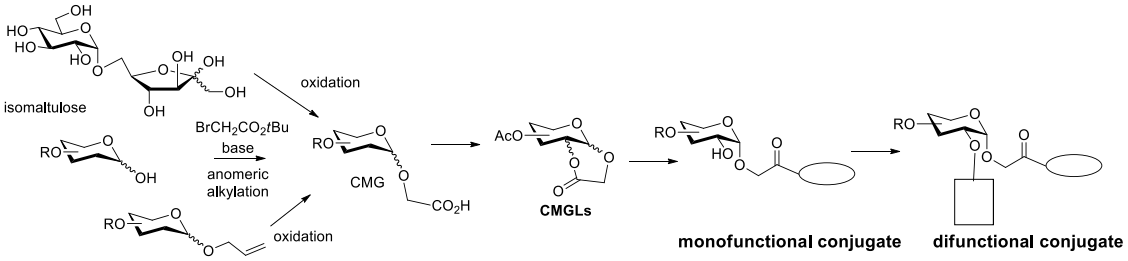

Fig. 1: The CMGL approach towards pseudo glycoconjugates.

A focus will be made on new liquid crystalline constructs having a glucoside head, a steroid unit and an alkyl side chain. These compounds change shape as a function of temperature depending on the length of the side-chain and that of the spacer. Lower transition temperatures are observed as the spacer is extended compared to direct connection. Regarding the effect of the side chain (Fig. 2), when it is long enough for overlapping with the steroid unit, the compound exhibited a hexagonal columnar phase at higher temperature while at lower temperature where the side chains are less dynamic a SmA phase was observed [6].

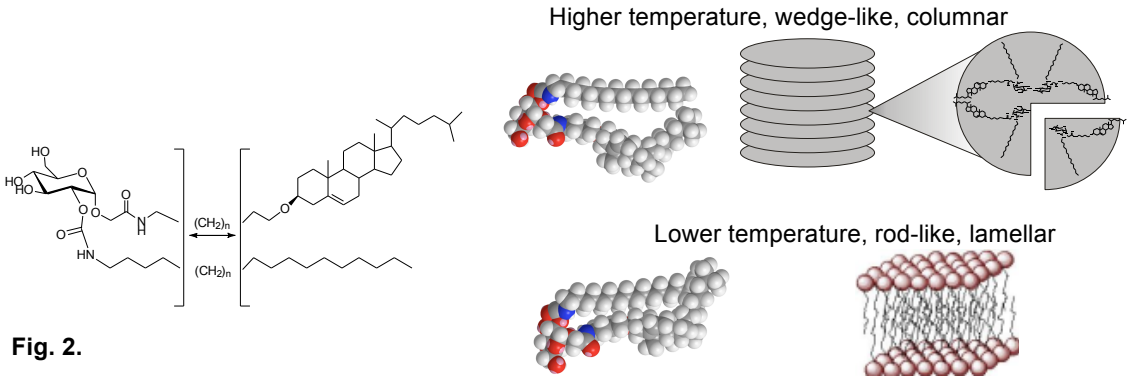

Fig. 2.

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BIOINSPIRED MATERIALS DERIVED FROM NATURAL SPECIES

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Energy crisis and environmental pollution have become major concerns to the public nowadays. Of the various possible methods, nature provides a blueprint for dealing with these problems and Bio-mimetic is an efficient strategy for material design inspired by nature. In this presentation, the recent progresses made in our lab are introduced typically. Firstly, I will present the general strategy to assemble man-made inspired materials templated with natural species such as bacterial, wood, green leaf and butterfly wing into natural species-shaped hierarchical architectures with unique properties such as efficient harvesting of light energy and photochemical hydrogen production. This concept may broaden the horizon for the design of artificial photosynthetic systems based on biological paradigms and provides a working prototype to exploit solar energy for sustainable energy resources. Secondly, I will describe the super black and ultrathin amorphous carbon inspired by anti-reflection architecture in butterfly wing, which to be a promising anti-reflection coating for various fields such as optical instruments, sensors and thermal detectors, and solar cells. This concept may shed new light on an old story of seeking for dark materials and might encourage people to look for more anti-reflection architectures in nature. Finally, I conclude and outlook by making a prospect on Bio-inspired and Biomimetic materials, which are the products of close conversations between human and nature and the product of close co-operation between scientists from diverse fields.

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THE BROAD IMPACT OF BIOLOGICAL INSPIRATION: FROM SUSTAINABLE ENERGY TO HEALTHCARE

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While the term "bioinspired" entered the scientific literature less than 20 years ago, for centuries biological inspiration has provided key paradigms for technological development.[1] This presentation will focus on the evolution of bioinspiration from biomimesis. Indeed, the evolution from biomimetic to bioinspired systems has proven essential for transferring fundamental discoveries from basic science to the applied aspects of advanced engineering.[1] Energy sustainability and healthcare (two of the most important challenges for the humanity) can benefit immensely from biological inspiration. The two parts of this presentation, therefore, will cover our recent advances in bioinspired electrets for energy conversion, and in bioinspired abiotic interfaces for facile and rapid clinical diagnosis.

In relevance to solar energy conversion, the first part of the presentation will focus on charge transfer mediated by biomimetic and bioinspired systems.[2] Protein-mediated electron-transfer processes sustain a broad range of redox functions in biological systems, such as respiration and photosynthesis. Therefore, such biological systems are indispensable "working" models for molecular design and for the development of materials for solar-energy-conversion and electronics applications.

Due to their ordered amide and hydrogen bonds, protein α-helices are some of the best known macromolecular electrets.[3] (Electrets, having ordered electric dipoles, are the electrostatic equivalent of magnets.) Local electric fields from such macromolecular electrets are on the order of 0.1 GV/m and cause degeneracy of charge-transfer states, key for directionality of electron entrainment.[4,5]

Examples will illustrate the role of solvent polarity, media viscosity and triplet formation for generating long-lived charge-separated states in biomimetic systems. Modulation of charge transfer by local electric fields, however, presents an alternative approach for achieving long-lived charge-separated states essential for energy conversion and storage. The presentation will cover our designs of bioinspired electrets and discuss their properties.[5,6]

The second part of the presentation will cover the utilization of bioinspired interfaces for rapid diagnosis of infectious diseases. Bacterial pathogens produce some of the most potent toxins known to man, and infectious diseases are still responsible for quarter of the human deaths worldwide.[7] The speed of detection and identification of microbial organisms often has life and death implications. PCR, cell culturing and other amplification pre-treatment steps, while time consuming, are key for detecting traces of pathogens in biological and environmental samples.

Recently, we introduced the concept of dynamic staining and demonstrated its unexplored capabilities for rapid identification of bacterial species. [8] Concurrently, we showed for the first time the ability of amyloid stains to selectively label bacterial cells and endospores in the presence of blood serum and in other biological and environmental samples. [9] For capturing and analysing traces of pathogens from blood and other biological samples, we utilized the natural propensity of bacteria to adhere to, to colonise and to infect tissues. Biofucntional interfaces, [10] based on carbohydrate ligands for bacterial adhesins, provided the means for selective extraction of traces of bacteria (e.g., $<10^3$ CFU/ml) from blood samples containing more than 10^{10} blood cells/ml, surpassing the sensitivity of the currently FDA-approved technologies for transfusion medicine.

The many different faces of biological inspiration provide an indisputable proof for the breath of its impact that extends considerably beyond its scientific and engineering implications.

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INTELLIGENT BIO-MATERIALS FOR TISSUE ENGINEERING AND NANOMEDICINE

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During the last decade, in the orthopaedic field the well-established approach for curing diseased bone parts, based on replacement with inert substitutes, has progressively given way to new regenerative approaches, based on the use of bioactive and biomimetic devices. However, technological limitations exist which slacken the establishment of regenerative therapies, since the regeneration of organized and multi-functional tissues (like osteo-cartilaginous anatomical regions) requires scaffolds able to show compositional and structural complexity.
The present work illustrates how bio-mineralization, an amazing natural process with which Nature has realised and optimised a profuse collection of living organisms endowed with astonishing abilities can be used to guide efforts for developing biomaterials for bone and osteochondral regeneration. In particular it will be illustrated how the self-assembling and bio-mineralization of natural polymeric fibres can be induced by reproducing the conditions of formation of new bone tissue in mammals, thus obtaining a collagen-based matrix where mineralization with nanoparticles of biomimetic apatite can take place. The reproduction of biomimetic conditions of bone synthesis allows to obtain hybrid constructs where the mineral phase is nucleated upon guidance by the chemical features and physical confinement imposed by the polymeric matrix, so that the mineral phase has physical, chemical and ultra-structural resemblance with mineral bone, thus providing very high osteogenic activity when implanted in vivo [1,2]. Besides, the possibility to vary the degree of mineralization allows to obtain multi-layer graded devices able to regenerate the different districts of the articular region (subchondral bone, mineralized and hyaline cartilage) [3,4]. Finally, pinning on the recent development, performed by our research group, of intrinsic superparamagnetism exhibited by hydroxyapatite nano-powders upon crystallographic and chemically controlled doping with Fe(II)/Fe(III) ions [5], it will be illustrated how bio-hybrid bone-like devices with intrinsic magnetic properties can be obtained; such devices can increasingly assist the osteogenic and angiogenic capacity of biologically inspired bone and osteochondral scaffolds, through magnetically-driven release of specific growth factors.
Moreover, the use of nano-structured phases able to penetrate inside cells for the treatment of tumors and/or for image diagnostics in nanomedicine is currently one of the most innovative and promising approaches. Intelligent nanoparticles able to be moved and driven by "magnetic guiding" and even to enter into the cells as non-viral vectors, are very promising materials for therapies and diagnostics in case of various cancer diseases.

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CELL SURFACE ENGINEERING WITH SYNTHETIC AND NATURAL LBL NANOSHELLS

Irina Drachuck, Olga Schepelina, Milana Lisunova, Chunhong Ye, Vladimir V. Tsukruk *

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Georgia Institute of Technology, Atlanta, USA

We report on designing highly permeable, gel, and robust nanoscale shells from synthetic [1,2] and natural [3,4] materials in order to conduct surface modification and protection of cells, [5] cell assemblies, [6] and anisotropic inorganic crystals. [7] Shells designed here were formed through a layer-by-layer assembly based upon hydrogen-bonding, ion pairing, and hydrophobic-hydrophobic interactions. These LbL shells can be reinforced via physical or covalent crosslinking by inclusion of nanoparticles, inducing local crystallization, or adding bifunctional crosslinking agents. These soft shells are exploited to control and tune the permeability and robustness of the coated structures and respective hollow replicae with complex shapes. We demonstrated that the pH-responsive outer coatings support high viability of the cells with minor effect of growth and dividing of cells especially if a cationic component is screened or completely removed. The important cell function to express green fluorescent protein was demonstrated to be preserved for a long time and can be controlled by external stimuli. In this presentation, we will discuss the sophisticated control in cell viability, the preservation of cell functioning, microcapsule shape preservation under variable pressure, pH-responsive behavior, and significance of core-shell morphologies for designing novel vehicles with tunable loading-unloading properties, enhanced robustness, and steric-guided self assembly.

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SELF-ASSEMBLED MICELLAR FLUORESCENT NANOOBJECTS FOR BIOIMAGING APPLICATIONS

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We propose here a novel miniemulsion process based on a phase inversion, without the use of surfactants and hydrophobic costabilizer. We chose a poly(ethylene oxide)-*b*-poly(acrylic acid) (PEO-*b*-PAA-TTC-C12) hydrophilic macro-RAFT agent in order to reach pegylated biocompatible and pH-sensitive auto-stabilized fluorescent nanoparticles. As such we are able to control the copolymerization of styrene with a fluorescent monomer in miniemulsion. BODIPY based monomer [1]. BODIPY methacrylate (BDPMA) was chosen as the fluorophore since it exhibits attractive and tunable spectroscopic characteristics. Since there is no surfactant and costabilizer and the synthesis is performed in water, the particles don't need any purification step before use in biological media.
This method is tunable since the nature of the encapsulated fluorophore can be changed, as well as the hydrophilic macroRAFT agent to get FNP of the same size. At last, thanks to the carboxylic acids present on the nanoparticles' shell, those one can be functionnalized by an amine-ended molecule. For instance, it can be a sensor such as fluoresceinamine to turn the nanoparticles into ratiometric pH-sensor. We are currently testing those nano-pH sensors in mammal cells. Tentative imaging in eukaryote cells and micro-organisms (*E.coli*) will be presented.

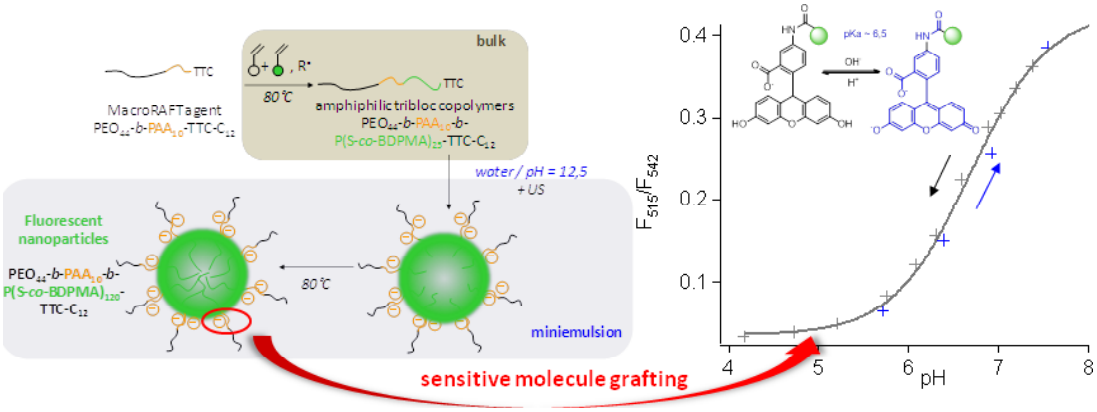

Fig. 1: novel miniemulsion process

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REACTIVITY AND CHEMICAL PROPERTIES OF METAL-OXO CORROLES: HOW DO THEY COMPARE TO PORPHYRINS?

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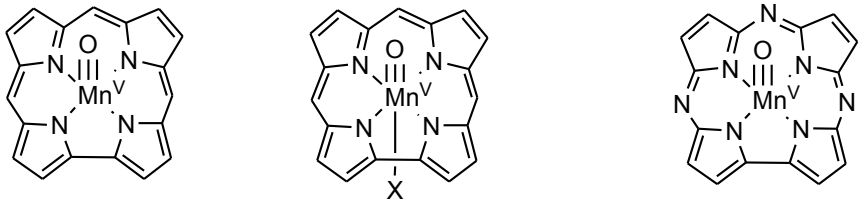
High-valent metal-oxo species are important catalysts in nature, and, for instance, act as the active species in a range of different heme and nonheme enzymes.[1] Furthermore, they are involved in a range of biotechnologically relevant reactions, including substrate hydroxylation (aliphatic and aromatic), epoxidation and heteroatom oxidation. As such they are well sought after, but despite many efforts in the field many questions regarding the activity of those oxidants remain. Biomimetic studies on metal complexes that resemble the active sites of enzymes help in the understanding of the fundamental components that drive the reaction mechanism. Thus, chemical structures with close resemblance to the heme/porphyrin (Por) in cytochrome P450 enzymes are the corroles (Cor) and corrolazines (Cz), Scheme 1, which lack one of the *meso*-CH groups of the heme (in corrole), whereas in corrolazines in addition the remaining *meso*-CH groups have been replaced by nitrogen atoms. Corrole and corrolazine macrocycles have overall charge 3– in contrast to the porphyrin charge of 2–. As a consequence these corrole and corrolazine units can stabilize metals in higher oxidation states than porphyrin, including Mn^{V}. In recent years we extensively studied the chemical properties and reactivities of iron(IV)-oxo and manganese(V)-oxo complexes with these ligand systems and variable axial ligands.[2–4] In particular, detailed studies focused on the reactivity patterns of $[Mn^{V}(O)(Cor)]$, $[Mn^{V}(O)(Cz)]$ and $[Mn^{V}(O)(Por)]^{+}$, as well as these complexes with additional axial ligands trans to the oxo-group. These studies highlighted a considerable rate-enhancement for hydrogen atom abstraction from substrates of >10,000 for a manganese(V)-oxo corrolazine complex, which were explained and rationalized with detailed computational studies. The studies highlight the potential of metal-corroles and metal-corrolazines in oxygen atom transfer reactions.



1$_{Cor}$ **[1-X]** **1**$_{Cz}$

X = F^{-} or CN^{-}

Fig. 1: Chemical structures of oxidants investigated with corrole (left) or corrolazine (right) ligand systems.

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NANOCOMPOSITE DESIGN OF ADVANCED MULTIFUNCTIONAL BIOMATERIALS

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Bioinspired nanocomposites are developed for various biomedical applications. These multicomponent materials can provide simultaneous drug delivery and bioimaging functions as theranostic systems. They can be synthesized with unique carrier materials that offer synergistic therapeutic effects with the drugs to be delivered. They can allow for the sustained delivery of growth factors to significantly enhance tissue regeneration.

In addition, nanostructure processing has been employed in creating synthetic cell culture substrates for the expansion and controlled differentiation of stem cells. Nanotechnology has also been combined with microfabrication to obtain biomimetic tissue engineering scaffolds and bioartificial assist devices. My laboratory has further developed nanosystems towards bioimaging, biosensing, diagnostics and drug screening applications.

NEW FUNCTIONAL AND SMART MATERIALS THROUGH MOLECULAR MODIFICATION AND BLENDING OF BIORELATED POLYMERS

Monica Bertoldo,[1] Simona Bronco,[1] Francesco Ciardelli,[1,2,*] Maria Beatrice Coltelli,[2,3] Andrea Pucci,[3] Giacomo Ruggeri,[3] Francesca Signori[1,2]

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Poly-α-aminoacids, polysaccharides and biorelated polyesters were modified by grafting or blending to innovative multiphase materials combining renewability and biodegradability with advanced functional properties.
Gelatine was successfully modified according to different routes namely crosslinking with 1,6-diisocyanatohexane (HDI) [1], side chain binding of hydrophobic florescent groups with 1-naphtylisocyanate (Npl) and grafting of isocyanate terminated polypropylenglycole monobutyl ether chains (PPG). The modified gelatine derivatives showed that the modification procedures all based on the reaction of isocyanate with reactive side chains provides materials with a large variety of water swelling and solubility properties.
Polypeptides from L-glutamic acid and L-lysine were modified by bonding of photochromic units, such as azobenzene [2] or spiropyran [3]. These photoresponsive poly-α-aminoacids show conformational and aggregation response to light irradiation and environmental conditions with high sensitivity.
Photoresponsive polysaccharide based on a precisely defined N-phthaloyl chitosan with covalent bound spiropyran, synthesized through “click” reaction, exhibited a distinct photochromic behavior with very slow thermal decay in the solid phase [4].
Aliphatic biodegradable poly(1,4-butylene succinate) [5] containing nanodispersed food-grade dyes show luminescence of excimers with dye concentration higher than 0.05 wt.%. On applying mechanical stress at r.t., the macromolecules reorganization breaks the dye selforganized structure, leading to the prevalence of the emission of the excited isolated chromophores. Moreover, kinetically trapped molecularly dispersed dyes in polymer melt quenched at 0 °C, gives films with optical response to temperature variation. Indeed the heating (T ≥ 50 °C) lead to the generation of thermodynamically stable aggregates among dye moleules , promoting the colour change of the material from monomer to excimer.
This approach was also successfully applied to polylactic acid based materials [5]. The thermal stimuli sensitive multiphase polymer system consisting of a mixture of poly(lactic acid) (PLA, 85 wt%) and poly(1,4-butylene succinate) (PBS, 15 wt%) was prepared by the controlled incorporation of moderate amounts (<0.2 wt%) of 4,4′-bis(2-benzoxazolyl)stilbene. Films obtained from the blend with less than 0.2 wt% of dye showed after melt mixing, the typical luminescence of molecularly isolated BBS chromophores (blue emission). Composite films containing 0.07 wt% of BBS (the highest concentration allowing dye molecular dispersion) appeared extremely sensitive to thermal solicitations when annealed at temperatures higher than PLA's T_g (>60 to 70 °C) leading to a clear change of the emission properties due to the occurrence of dye aggregation. Thermal analysis by DSC showed an evident connection between blend morphology features and luminescence response.
The optical response of the subject smart biorelated materials are discussed with reference to the bonding and interactions between the original biorelated macromolecule and the grafted groups with particular reference to their role in determining the coinformation and sovramolecular organization of the hybrid materials prepared.

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BIOMIMETIC ACTIVATION OF MOLECULAR OXYGEN BY NON-HEME Fe(II) COMPLEXES WITH TRIPODAL NITROGEN LIGANDS: A FUNDAMENTAL APPROACH

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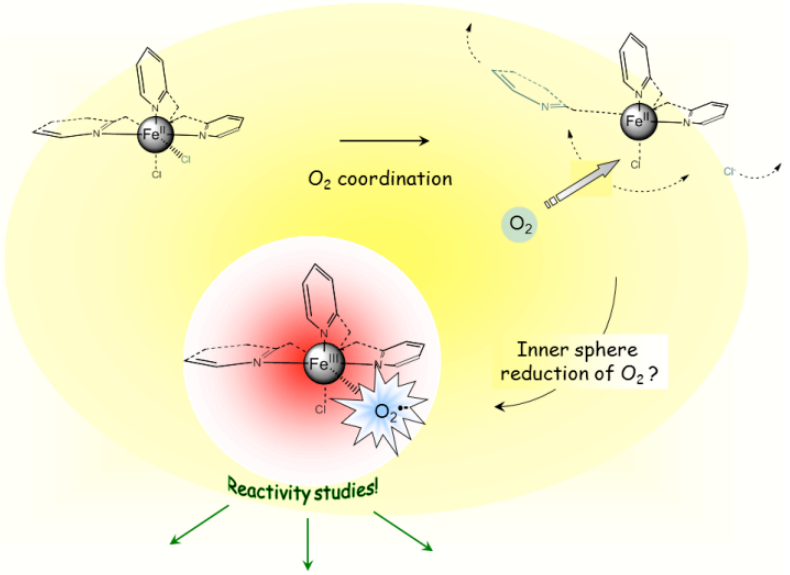
Mononuclear non-heme iron centres are involved in many major oxidation processes occurring in Nature, and their ability to catalyze oxidation reactions in mild conditions renders these active sites particularly interesting in our current global context. In the field of oxidation catalysis, the biomimetic approach which considerably developed over the last 25 years ago, is still considered as a promising answer to the current concern in terms of sustainable growth and energy sparing. With time, biomimetic systems which originally exhibited a low efficiency have become more attractive, being now used in conversions of more sophisticated substrates than simple alkanes. Yet, in most of the cases is dioxygen replaced by its reduced peroxidic forms. Few simple mononuclear complexes with tripodal ligands that are able to react with molecular oxygen are known, however the metal is in that case generally activated by a non-innocent exogenous ligand (thiolate, catecholate or α-ceto carboxylate). Obviously, focusing on the reactivity of simple mononuclear iron complexes versus molecular oxygen is still extremely challenging.



$FeCl_2$ complexes with TPA-type ligands display moderately positive Fe^{II}/Fe^{III} redox couples: they are *a priori* not supposed to reduce molecular oxygen. But $FeCl_2$ complexes with TPA-type tripods are definitely oxygen-sensitive, and undergo clean conversions, most of the time into μ-oxo diferric species. Additionally and depending on its structure, modification of the ligand may be observed. It seems that accessibility of O_2 to the metal centre, as well as Lewis acidity of the iron represent crucial parameters with respect to the oxygen sensitivity. We shall present indirect evidence for coordination of O_2 to the iron centre, leading to the reductive activation of molecular oxygen. We shall also discuss the characterization by a broad array of spectroscopic techniques of a transient species obtained upon oxygenation of a Fe^{II} complex, which may be described as an $[Fe^{+III}]$ $[O_2^{\cdot-}]$ species. We shall finally try to draw a perspective for future extension of these studies to more practical outcomes.

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VEGETABLE-BASED BUILDING BLOCKS FOR THE SYNTHESIS OF RENEWABLE POLYMERS

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In our daily life, we are unavoidably, constantly surrounded with polymer materials. To date, most of the monomers that are used to prepare polymers are derived from petroleum (fossil) sources. These fossil resources particularly, petrol and natural gas, will arguably be depleted within one or three generations. Due to this depletion and to escalating prices, polymer chemists have turned their attention to obtain monomers and polymers from renewable resources [1]. Vegetable oils have a large potential to provide renewable chemicals, thanks to their availability, sustainability and biodegradability. Vegetable oils bring different functional groups (ester functions, double bonds) that can be derivatized to design novel well-defined functional building blocks for the synthesis of speciality polymers. Many recent efforts have been directed towards replacing entire or part of petroleum-based polyols as main precursors of polyurethane (PU) and polyester materials.

First, this presentation will focus on the synthesis of new diols, from castor and sunflower oils, containing ester, esteramide and amide linkages through transesterification, amidation and thiol-ene reactions. A series of amorphous and semi-crystalline polyurethanes [2], polycarbonates [3] and polyesters [4] have been obtained that exhibit different thermo-mechanical features with respect to the diol nature. The relationship between the diol molecular structure and the properties of the so-formed polyurethanes, polyesters and polycarbonates will be presented and discussed in the light of thermo-mechanical and X-ray analyses as well as tensile experiments.
Second, this presentation will present non-isocyanate and greener pathways to PU. A first route deals with the reaction between diamines and biscarbonates, the latter obtained by reaction of the fatty ester bis-epoxides [5]. A second route concerns a unique approach to the synthesis of PU through the self-polyaddition of new monomers containing acyl azide-hydroxyl functionalities [6]. The structure-property relationship of these various monomers and the respectively so-formed polyurethanes will be also discussed during the presentation.

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MOLECULARLY IMPRINTED POLYMERS: BIOMIMETIC SYNTHETIC ANTIBODIES

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Molecularly imprinted polymers (MIPs) are synthetic receptors that specifically recognise target molecules. They are highly cross-linked polymer networks that are synthesized through the polymerization of monomers bearing suitable functional groups, in the presence of the target molecule, which acts as a molecular template. After removal of the templating molecule, the polymer contains three-dimensional binding sites that are complementary to the template in terms of size, shape and chemical functionality. The MIP can therefore recognize and bind the target with an affinity and selectivity similar to an antibody (Fig. 1, top). They have found applications for example as antibody mimics in immunoassays, as recognition elements in biosensors, or in affinity separation. This talk will cover recent advances in molecular imprinting technology, with special emphasis on the the detection of proteins. In particular, the use of MIP nanogels as enzyme inhibitors, MIP "nanograss" obtained by a nanomoulding procedure on sacrificial porous supports, and single MIP nanosensors based on metal nanocomposites and surface-enhanced Raman spectroscopy will be presented. New approaches allowing for the controlled synthesis of MIP nanomaterials by living radical polymerisation methods will be discussed, in particular the synthesis of protein-size, soluble MIP nanogels (Fig. 1, bottom).

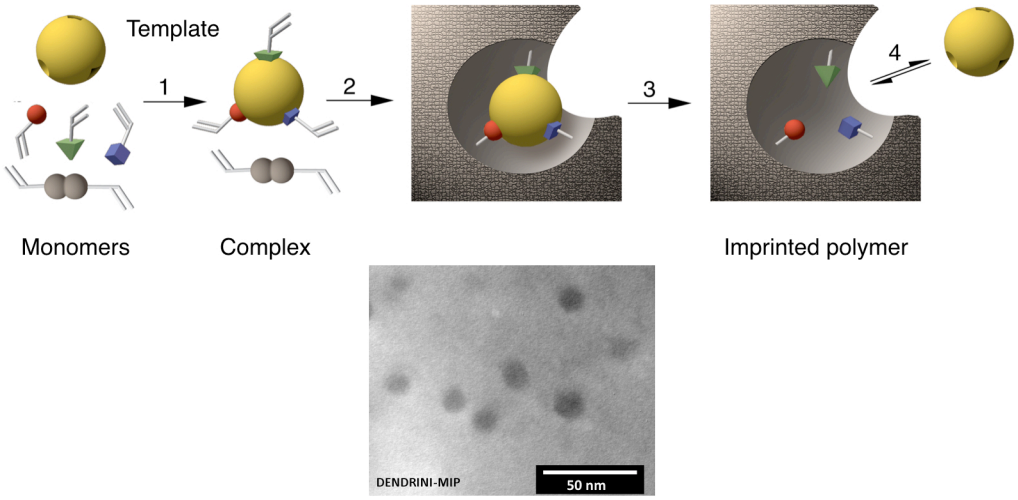

Fig. 1: Top: General principle of molecular imprinting: 1, complex formation between template molecule and functional monomers, 2, polymerization in the presence of cross-linking monomer, 3, liberation of the binding cavity, 4, specific binding of the target molecule. Bottom: Soluble MIP nanogel particles obtained by polymerization with a dendritic multiiniferter (mean diameter: 19 nm).

POLYDIACETYLENE – A UNIQUE CHROMATIC BIOMIMETIC POLYMER FOR MEMBRANE, BACTERIAL, AND CELLULAR SENSING

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Polydiacetylene (PDA) is a conjugated polymer exhibiting unique color and fluorescence properties. In particular, the polymer can be incorporated within diverse membrane-mimic environments and undergoes dramatic blue-red transformations accompanied by fluorescence emission which are induced by varied external molecular stimuli. In this context, PDA constitutes a sensitive chromatic sensor for diverse biological molecules and processes. In this talk I will present highlights from our work with PDA over the past few years. I will describe the use of PDA in varied configurations, including small and giant vesicles, Langmuir monolayers, sol-gel host matrixes, and others, and the application of this intriguing biomimetic sensing platform for analysis of membrane processes, bacterial detection, and cell-surface interactions *in situ*.

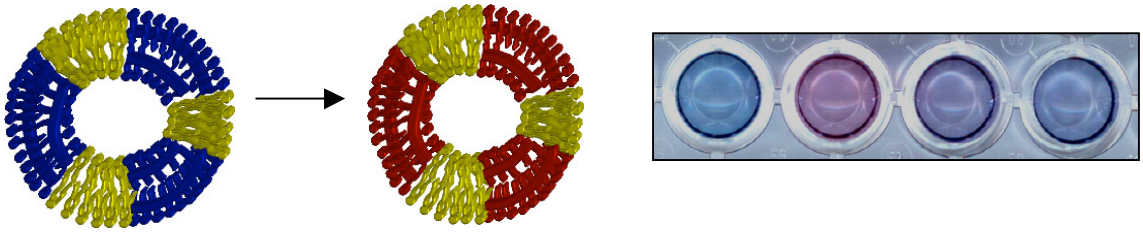

Fig. 1: Colorimetric transitions in lipid/PDA vesicles.
Left: schematic depiction;
right: scanned image of blue (control) and red (transformed) vesicle suspensions.

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BIOMIMETIC MORPHOGENESIS AND STRUCTURE OF CALCITE STATOLITHS (OTOCONIA): AN APPROACH TOWARDS DEEPER UNDERSTANDING OF A BIO-SENSOR AND ITS FUNCTION

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The inner ear of vertebrates contains a complex arrangement of enclosed sacs and channels which are the sites of the senses of balance and hearing. Parts of these sensory systems are called maculae acting as gravity receptor organs responding to linear accelerations. [1] The sensory transduction depends on the inertial mass of a calcium carbonate biomineral (so-called statolith) which, in case of fish and amphibians consist of aragonite or in rare cases even vaterite (so-called otoliths), while reptiles, birds and mammals produce the calcite modification (so-called otoconia). Otoconia (ear dust; µm-sized) show a barrel-shaped habit with triplanar faceted ends [2-4] and undergo only little changes with time. The perculiar shape of otoconia as well as their inner structure and the resulting biofunctionality are far away from being fully understood up to now. The same is true for their shape development (morphogenesis).

Our recent investigations [5] contribute to these essential questions by a close biomimetic approach (via double-diffusion and growth in gelatine-gel matrices) and are focused on the shape development of the complex composite architecture resembling all the structural details which are known from biogenic otoconia up to now. The peculiar morphogenesis as well as the decalcification behaviour of the biomimetic otoconia give rise to deeper understanding of their functionality responding to linear accelerations. On the biogenic side especially human otoconia are used to draw comparisons. [6,7]

The knowledge on morphogenesis, inner architecture and chemical composition of the biomimetic and the biogenic composites may help for the development of repair-strategies, even for human otoconia.

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POLY(ETHYLENE OXIDE) BASED MATERIALS : FROM SYNTHESIS TO BIOMEDICAL APPLICATIONS.

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Poly(ethylene oxide), (PEO) is an hydrophilic polymer which exists in various forms and structures and exhibits specific solution and solid state properties. Furthermore, the remarkable biocompatible properties of this polymer have already led to a wide number of biomedical applications.
The first part of the presentation discusses some general aspects of poly(ethylene oxide). The synthesis and the characterization of a series of PEO or PEO based macromonomers fitted, at one or both chain ends, with allyl, undecenyl or methacrylate end- groups will be presented in the second part.
Multifunctional poly(ethylene oxide) (PEO) star-polymers constitute a particularly promising class of materials since they represent models for physico-chemical studies, and variable building blocks for the synthesis of structured soluble polymers for amphiphilic networks. Their synthesis refers in most cases to the so-called “core-first” method, in which living cores are used for the anionic polymerization of oxirane. The present work discusses also the synthesis and the properties of star-shaped PEO’s fitted with an octafunctional silsesquioxane core.
Hydrogels based on PEO have been shown to be suitable materials for numerous applications. Among the different approaches to design such hydrogels, the homopolymerization of well-defined bifunctional PEO macromonomers represents a promising one. In such systems, crosslinking is achieved upon free radical polymerization of the methyl methacrylate units located at both chain ends. Gels were synthesized over a large range of molar masses of the macromonomer precursor. They were investigated swollen to equilibrium in THF, toluene or in water. The mechanical properties of the networks were studied and compared to those of hydrogels obtained by hydrosilylation.
The final part concerns the application of these hydrogels as semi-permeable membranes or as a support for the growth of nervous cells. PEO hydrogels were also tested with respect to their ability to serve as a template for the survival and the growth of hepatocytes.

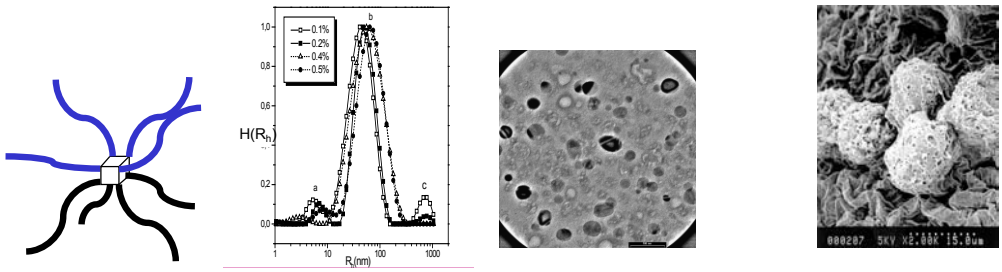

Fig. 1 : SEM images

POLYMER BRUSHES: TUNING THE BIOLOGY-MATERIALS INTERFACE

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Polymers brushes are ideal materials for interfacing with biological systems as they share many of the same molecular components and properties. [1] Polymer brushes, or surface tethered polymers, provide remarkable screening power in shielding a substrate from the environment through both steric and charge interactions. [2] However, the majority of biomolecular species will still non-specifically bind to polymer brush surfaces unless some care is given to molecular design. [3] We have recently explored the effect of brush thickness on non-specific binding and cellular attachment. Several polymer brush systems are described to control interaction of biomacromolecules and cells by design of specific and non-specific interactions in polymer brush architectures. “Grown from” and block copolymer brushes [4] are discussed, both of which provide excellent substrates for study of brush surfaces. Nanostructured polymer „carpets“ are also reported. Examples of polymer brushes used for sensor creation and for investigation of cellular interaction are provided. Brushes used in non-fouling coatings tailored for marine applications and in which amphiphilic structures play an important role are also described.

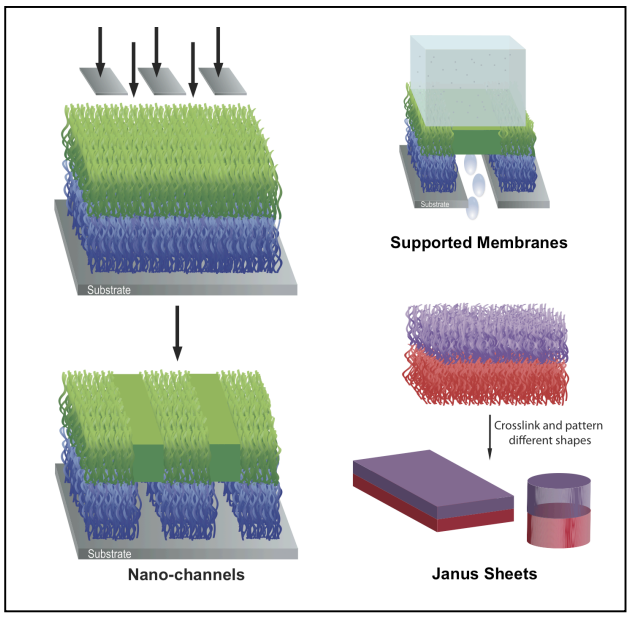

Fig. 1: Polymer Brushes and possible nanostructures derived from them

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BIO-INSPIRED CATALYTIC RADICAL-TYPE TRANSFORMATIONS

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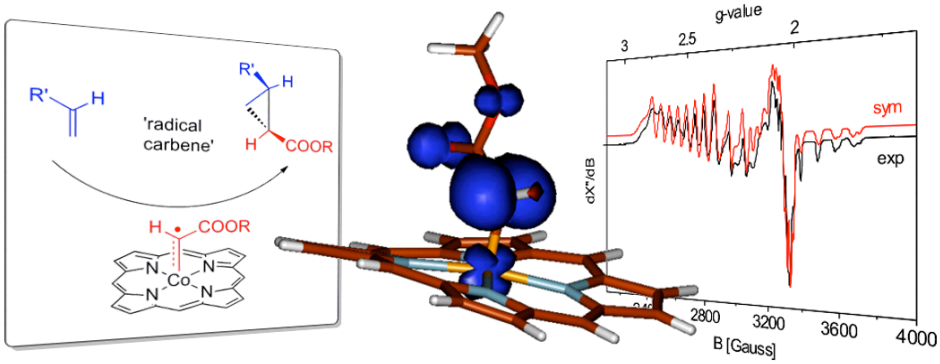
Radicals are intrinsically reactive, and were long believed to be *too reactive to be selective*. However, in the coordination sphere of transition metals highly selective radical-type processes are certainly possible. In fact, radical-type reactions are tremendously important in several bio-synthetic pathways mediated by metallo-enzymes. Nature solves its most difficult and most interesting bio-synthetic problems with radical-reactivity. Yet, despite their radical-nature, these reactions proceed with ultrahigh precision and selectivity.
Inspired by such intriguing catalytic radical-type transformations mediated by metallo-enzymes, we recently started to investigate new catalytic radical-type transformations mediated by synthetic (open-shell) organometallic catalysts. Special interest in such open-shell organometallic species comes from their expected higher and different reactivity compared to their closed-shell counterparts, and these 'metallo-radical complexes' may well allow us to steer and control radical-type reactions.[1, 2]



In this contribution we will discuss the available bio-inspired tools to steer and control (ligand) radicals within the coordination sphere of transition metals, and disclose their initial application in carbene- and nitrene-transfer reactions.[3,4] Reactivity studies, EPR spectroscopy and complementary DFT calculations are used to unravel the open-shell pathways of the paramagnetic Co^{II}, Rh^{II}, and Ir^{II} species.

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BIOINSPIRED SYSTEM FOR THERMAL ENERGY MANAGEMENT

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Thermal energy is one of the most abundant energy forms currently used in industrial processing and household operations. Efficient thermal energy management is a critical approach in lowering the energy consumption, reducing the carbon footprint and greenhouse gas release, and improving the overall system level efficiency. In one particular area, high performance electronics, thermal energy becomes specially challenging to control and prevents the further performance improvement due to the failure of the components at high temperature. This presentation will discuss the issues related to the thermal energy management in high performance electronics, and provide examples of solving these issues. GE's effort in building bioinspired super-thermally conductivity thermal ground plane will be discussed in the presentation. The thermal ground plane system is capable of conducting heat at order of magnitude better than copper, which is the most common material used for the thermal energy managemetn in the current electronic devices and systems. The bioinspired design and engineering also enables the operation of the thermal ground plane system at >12 times of gravity acceleration condition, and provides potential of reduced footprint and matched coefficient of thermal expansion. Both the learning in developing the thermal ground plane system and other possible applications of such bioinspired system in thermal energy management will also be discussed in this presentation.

Oral Abstracts Session A

BIOINSPIRED MULTI-FUNCTIONAL COATINGS: COMBINING SURFACE CHEMISTRY AND TOPOLOGY

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Since early times, scientists and engineers have tried to mimic Nature to design synthetic materials and devices with advanced properties. One of the most pursued natural phenomena is the ability to manipulate water at interfaces in the same manner that living organisms do: Either they repel, attract, absorb or transfer water; it is always done in a controlled way, to guarantee the necessary conditions for their vital functions, *e.g.* feeding, growing, moving or reproducing.
Nearly all surfaces we use nowadays have a coating for protection or aesthetic purposes. One of the most important roles of coatings is setting the desired water interaction at interfaces. Hydrophobic coatings have been extensively used for low-adherence and water repellent surfaces (*e.g.* protective coatings on cars, airplanes or electronic devices). On the other hand, hydrophilic coatings have found application in areas where the contact with fluids (aqueous solutions) plays a major role (*e.g.* contact lenses, catheters and many other medical devices).
Currently, the coatings field faces new challenges towards the design of multi-functional surfaces, which should not only exhibit a specific wettability [1] but also respond in a selective way to changes in the environment. Also in this case, Nature surfaces revel the secret: the combination of the proper surface chemistry and topology leads to multi-functionality and superior properties [2], *e.g.* the self-cleaning behavior the lotus leaves which results from its superhydrophobicity [3] or the spider-silk fibers ability to absorb and release water in a controlled way due to its surface characteristics [4] (Fig. 1). Furthermore, these surfaces have an additional and remarkable feature which is highly desired for synthetic surfaces: they self-regenerate every time a surface damage occurs, ensuring the prevalence of the functionality throughout their living period.
Herein, we present several examples [5],[6] on how the combination of surface chemistry and topology can be used to develop multifunctional “smart coatings”: *e.g.* self-healing and hydrophobic (or superhydrophobic) polymer coatings or coated-cotton fibers with reversible wettability and water absorption and release behavior.

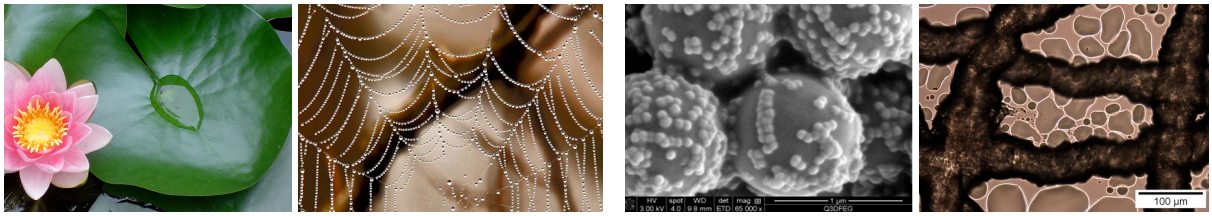

Fig. 1: (*left*) Nature inspiration: Water droplets on a Lotus-leaf and on a spider web; (*right*) Synthetic materials: superhydrophobic self-cleaning and self-healing coating and coated-cotton fibers releasing water droplets.

The multi-functional surfaces (coatings) reported here may find application on advanced technological fields of the utmost importance, *e.g.* high efficiency solar panels with self-cleaning coatings which do not accumulate dust and self-repair surface scratches or damage; or cotton fabrics which collect and release water in a controlled manner and can be used for fresh water collection and purification.

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REACTIVE MONOLAYERS: TEMPLATES FOR BIOMOLECULES AND INTERFACES FOR TECHNOLOGY

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Self-assembled monolayers have been the workhorse for nanotechnology since a few decades. They constitute an interface and "interphase" between a substrate and the "outside world". Their functions are by far not only the basic types such as substrate protection, anchoring and tuning of hydrophilicity, but have progressed into ever increasing added value ranging from molecular recognition (e.g. for sensing), molecular construction, biomolecular orientation, electronic transport, signalling, etc.
Reactive monolayers, i.e. monolayers that have some reactive moiety at the headgroup that allows further functionalization, form a subclass that is extremely useful for molecular (nano)fabrication. The reactivity of such monolayers can be the same or drastically different (faster or slower) than of their solution analogs.
The current presentation focuses on examples that range from biomolecular templates to technological applications. The development of reactive platforms that signal attachment reactions occurring onto them is useful for biomolecular arrays. Examples will be shown of protein patterns, using a thiol-reactive platform [1]. Surface gradients are being developed and used to address and map reactivity profiles on surfaces on reactive monolayers [2]. Additionally, an example using paramagnetic complexes to make spintronic devices is shown [3].

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A NEW ALS TYPE MULTI-RESPONSIVE LOW-MOLECULAR-WEIGHT ORGANOGEL BASED ON SALICYLIDENE SCHIFF BASE

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Recently, smart materials based on stimuli responsive low-molecular-weight gelators (LMWGs) have become a new focus, owing to their potential applications in photo switches, sensors, molecular logic gates, and other functional materials [1,2]. As a kind of multi-responsive molecules, salicylidene Schiff bases have recently received particular interest because of their excellent photochromic, thermochromic, solvatochromic and their response to metal ions, anions and pH [3,4]. In past few years, there have been developed several Schiff base derivatives with gelation abilities and other corresponding properties. However, to the best of our knowledge, the metal ions as well as anions responsive gel based on salicylidene Schiff base has rarely been reported.

In this work, a new ALS type gelator **1** based on Salicylidene Schiff base has been synthesized and demonstrated. Gelator **1** can gelate many solvents by self-cooling or ultrasonic processing. Scanning electron microscopy (SEM) reveals that the xerogels of stable gels have fibrillar microstructure. FTIR confirms the existence of intermolecular hydrogen bonding in the gel. Furthermore, the gel of **1** exhibits an enhanced fluorescence emission which is ascribed to the combination of inhibition of the intramolecular rotation and the formation of J-aggregates. Thermochromism is observed which can be explained by the equilibrium between the enol (OH) and the keto form (NH). The gel of **1** responds to many transition metal ions by undergoing gel-sol translation and color change. Particularly, the gelator **1** shows a selective fluorescence response to Zn^{2+} in both solution and gel state. Moreover, the gel also shows a good anion responsive property in aprotic solvent acetonitrile. Overall, we reveal the multiple stimuli-responsive behaviors of the salicylidene Schiff base gel, and the new gelator may probably have a potential application as a multifunctional material.

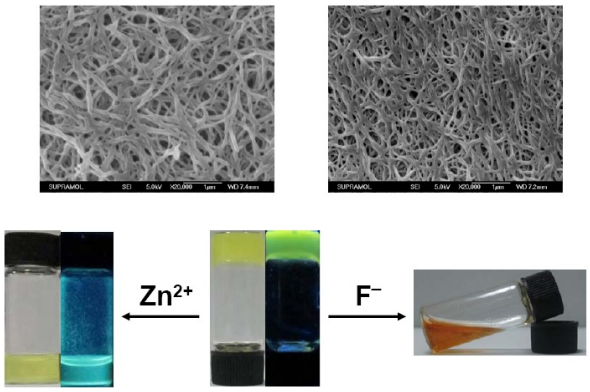

Fig.1: SEM images of the 1 xerogels in ethanol (left) and acetonitrile (right); Color and fluorescent changes of gel 1 to Zn^{2+} and F^-.

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ELABORATION AND RHEOLOGICAL STUDY OF MAGNETIC SENSITIVE NANOCOMPOSITES BIOPOLYMER BASED NETWORKS

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[1]*Univ Paris Diderot, Sorbonne Paris Cité & CNRS, MSC, Paris, France*
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In the past few years there has been increased interest in the development of stimuli-responsive polymer materials of emerging applications. In particular magnetic polymer networks are a new class of soft polymer materials with the properties controlled by magnetic field. In this context we elaborated new magnetic sensitive nanocomposites bio-based polymer networks by introducing magnetic nanoparticles in uncrosslinked or crosslinked aqueous solutions of sodium alginate. Sodium alginate is a linear copolymer containing sequences of units β-1 ,4-D-mannuronate (M) and α-1, 4-L-guluronate (G) in varying proportions. Each unit M or G beared a carboxylate group (COO^- ionized form) leading to a negatively charged polyelectrolyte in the media of neutral or basic pH. Iron oxide nanoparticles (average size around 10 nm) were synthesized on the basis of hydrolysis and condensation reactions of iron acetate in a polyol solvent and water. The functionalization of these nanoparticles was achieved by using two bifunctional organic ligands that grafted to the surface of the nanoparticles either by complexation of ions Fe^{3+} or by linkages Si-O-Fe through sol-gel process. The development of a new original device allowed the measurements of mechanical properties under continuous magnetic field in order to determine structure and dynamical properties at various external conditions [1]. An example of shear rate dependence of the shear viscosity for an aqueous alginate solution (C_{alg} = 18g.L^{-1}) with magnetic nanoparticles (Φ_{NP} = 0.5%) is given on Figure 1. The most interesting point is the increase of viscosity for shear rate lower than around 10s^{-1} while all the curves superpose for higher values of shear. The explanation is the formation of magnetic field induced structures due to interactions between magnetic nanoparticles and polymer chains in a direction perpendicular to the shear rate (see the insets showing microscopic observations of the aqueous solution of alginate with magnetic nanoparticles without magnetic field and when a magnetic field is applied) with a predominant magnetic effect. On the contrary this magneto-viscous effect tends to disappear when the shear rate prevails.

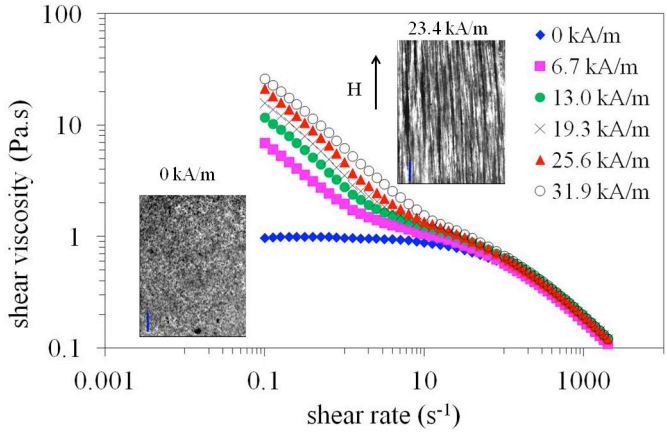

Fig. 1: Shear rate dependence of shear viscosity at various magnetic field values for aqueous alginate solution In the insets are showed microscopic observations of the solution without magnetic field and when a magnetic field is applied (scale bar: 100 μm) .

We have clearly demonstrated reversible modulation of low shear and viscoelastic properties of new magnetic sensitive nanocomposites biopolymer-based networks opening new perspectives of applications for these materials.

[1] The project was funded by 7th Framework Programme of the European Communities: http://www.physique.univ-paris-diderot.fr/magbiomat

BIOMIMETIC $CaCO_3$ MINERALIZATION MEDIATED BY HYPERBRANCHED POLYMERS: MORPHOLOGY EVOLUTION AND POLYMORPHIC TRANSFORMATION

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Aggregation-driven mesocrystal formation with specific size, shape, morphology and highly ordered superstructure is demonstrated an important non-classical pathway to create biominerals and construct advanced functional materials [1]. Calcium carbonate ($CaCO_3$) is the most abundant biological minerals existing in three anhydrous crystalline polymorphs, i.e., vaterite, aragonite, and calcite with increased stability [2a], the mollusk shell nacre mainly composed of aragonite and organic components (acidic proteins and polysaccharides) showed nanoscale "brick-motar" lamellar superstructure with superior mechanical properties [2b, 2c]. Due to their ease in synthesis, hyperbranched (hb) polymers typically exhibiting some similar features as the perfectly branched dendrimers [3a,3b], may serve as alternative of dendrimers in many fields [3c].

Following the investigation of biomimetic crystallization of $CaCO_3$ in the presence of functionalized hb polyesters or polyglycerols [4], here we present the morphology evolution and polymorphic transformation of $CaCO_3$ through a bioinspired ambient long-term incubation process in their mother solution in the presence of sulfonated hyperbranched polyesters, regular polycrystalline calcite lamellar morphology have been achieved through a polymer-mediated aggregation crystallization mechanism after a long incubation time as show in Fig. 1. The combination characterization of FE-SEM, TEM, XRD, FTIR, DLS revealed the morphology evolution from nanoparticle-aggregated micrometer-scale vaterite spheres into regularly stacked lamellar calcite polycrystalline materials, via a hexagonal vaterite mesocrystal intermediate and a solid-solid phase transformation as briefly illustrated in Figure 1.

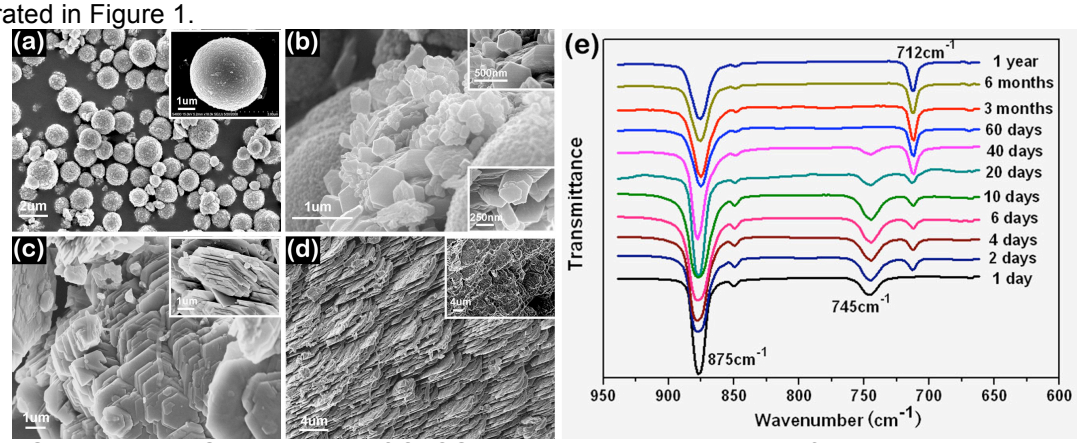

Fig. 1: Some typical SEM images of $CaCO_3$ particles mediated by sulfonated hb polyesters with morphology evolution from vaterite spheres to Nacre-like lamellar superstructures for different incubation time of (a) 24h, (b) 20days, (c) 3 months, (d) 6months, and (e) FTIR spectra of the harvested same batch $CaCO_3$ particles with incubation time from 1 day to 1 year.

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REVERSIBLE SWITCHING BETWEEN SUPERHYDROPHOBIC STATES ON A HIERARCHICALLY STRUCTURED SURFACE

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[3]*Division of Pharmaceutical Chemistry, Faculty of Pharmacy, University of Helsinki, Finland*
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Nature offers exciting examples for functional wetting properties based on superhydrophobicity, such as the self-cleaning surfaces on plant leaves and trapped air on immersed insect surfaces allowing underwater breathing. They inspire biomimetic approaches in science and technology. Superhydrophobicity relies on the Cassie wetting state where air is trapped within the surface topography. Pressure can trigger an irreversible transition from the Cassie state to the Wenzel state with no trapped air — this transition is usually detrimental for non-wetting functionality and is to be avoided. Here we present a new type of reversible, localized and instantaneous transition between two Cassie wetting states, enabled by two-level (dual-scale) topography of a superhydrophobic surface, that allows writing, erasing, rewriting and storing of optically displayed information in plastrons related to different length scales [1].

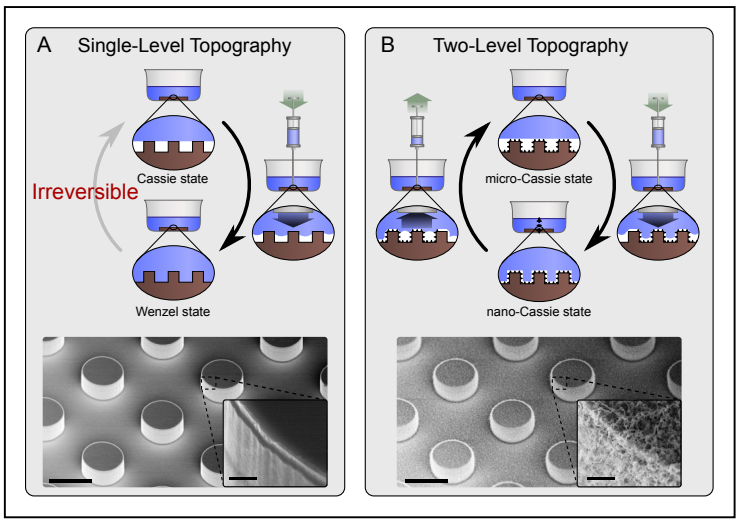

Fig. 1: Wetting states and transitions between them on surfaces with different topographies. (A) With single-level topography, positive Laplace pressure causes a transition from the Cassie to the Wenzel state. The transition involves wetting of the whole solid surface and is irreversible in most cases. (B) Hierarchical topography. Nanofilaments suppress the transition to the Wenzel state and positive Laplace pressure will cause a transition to the nano-Cassie state instead, where wetted solid area remains small due to the plastron in the nanofilament layer. This transition can be reversed by negative Laplace pressure.

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ORTHOGONAL MUSSEL INSPIRED SURFACE MODIFICATION

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Mussels are adapted to survive environments of tidal zones. They attach to any material (i.e. rocks, wooden piers, metal bridges, ships) even under harsh and turbulent conditions. The anchoring is only achieved by an extraordinary adhesion system, namely the mussel byssus which is composed of a bundle of extracellularly secreted collagenous threads that are glued to the material by an adhesive plaque at their distal ends [1]. The threads show amazing stiffness and at the same time high elasticity and superadhesion in a wet environment.
Messersmith and coworkers have investigated mussels and their surface adhesion strength previously. These authors discovered that the coexistence of amino and catechol functional groups, provided by 3,4-dihydroxyphenylalanine (DOPA) and lysine peptide sequences in the mytilus edulis foot protein 5 (Mefp-5), are the essential factors responsible for their exceptional adhesion [2]. Emerging from these findings was the realization that dopamine and DOPA could feasibly serve as a precursor to biomimetic mussel-like adhesives *via* dopamine- or DOPA- self-assembly because these compounds carry both catechol and amino functional groups, which were identified on the interfacial location of Mefp-5 [1].
Apart from the self-assembly of dopamine or DOPA to imitate mussel adhesives and, hence, to provide a surface coating, several alternative surface attachment paths for these substances have been proposed [3]. Following the self-polymerization of dopamine or DOPA, functional groups – such as amino or hydroxyl groups – are still available on the surface of dopamine or DOPA coated materials. These functional groups can therefore be employed as sites for further surface modification. Based on these findings we would like to present in the current study the synthesis of a new functional DOPA precursor which contains, on the one hand, the catecholic functionalities for bioinspired surface attachment and on the other side a functionality ready for subsequent transformation under maritime conditions. Characterization of the mussel-inspired coatings was carried out via X-Ray photoelectron spectroscopy (XPS), FT-IR spectroscopy and FT-IR microscopy. Our aim is mimicking the adhesion of mussel byssus threads via a synthetic route and to extend the unique properties of DOPA by synthesizing hybrid biomaterials.

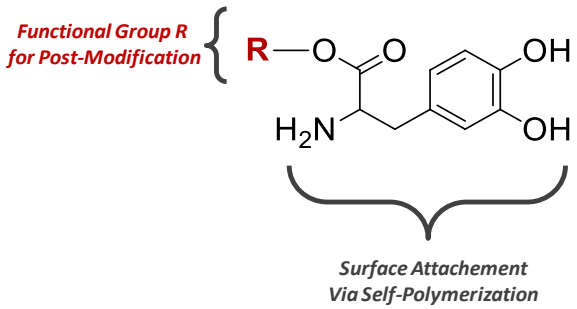

Fig. 1: Synthetic strategy for modular surface modification under maritime conditions

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HYGROSCOPIC MOVEMENT IN GERANIACEAE- DIVERSITY, STRUCTURE AND EVOLUTION

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Hygroscopic movement is a passive form of movement invoked by dead plant tissues with highly specialized structural characteristics. Geraniaceae is a family of flowering plants characterized by seed dispersal mechanisms relying on this type of movement. In this plant family, long narrow appendages (awns) are attached to seed capsules. After maturation, these awns, that are dead tissues, respond to humidity changes, contracting and deforming to facilitate the dispersal of the seeds. The awns within the Geraniaceae family display several types of deformations, mainly bending and coiling, with coiling being the most common. In this work we elucidate the structural variation leading to the different functionalities of the awns. We chose five representative members of the three main genera in the Geraniceae family; *Erodium*, *Pelargonium* and *Geranium*, that display different awn deformation (Fig. 1). We characterized the cell wall nanostructure by small angle X-ray scattering as well as polarized light microscopy, using the LC-PolScope system. This system that has been widely implemented in cytoskeleton studies has been rarely used in the investigation of plant cell wall organization. Here we show this system's ability to elucidate spatial aspect in the information obtained from the X-ray analysis (Fig. 2). We found that while the bending awn relies on a bi-layered structure similar to bilayer thermometers, coiling awns rely on an unusually tilted cellulose microfibrils organization within the cell walls [1]. We show that specific variation in the layering of the awn, along with the change in the cell wall nanostructure, controls the dry awns topology and adjusts the dispersal mechanism functionality to the changing environmental conditions.

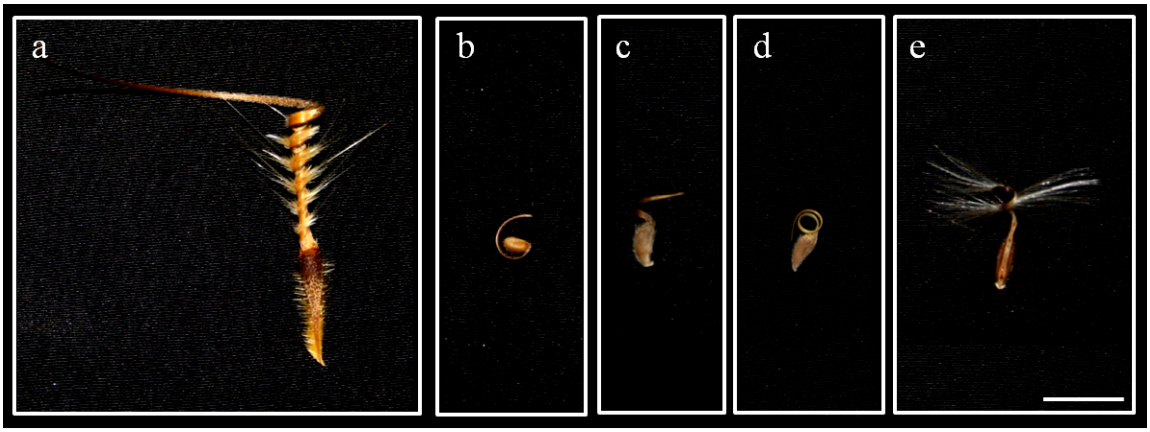

Fig. 1: Geraniaceae dispersal units. (a) *Erodium gruinum*. (b) *Geranium pusillum*. (c) *Geranium dolomiticum*. (d) *Geranium reflexum*. (e) *Pelargonium peltatum*. (Scale: 1 cm)

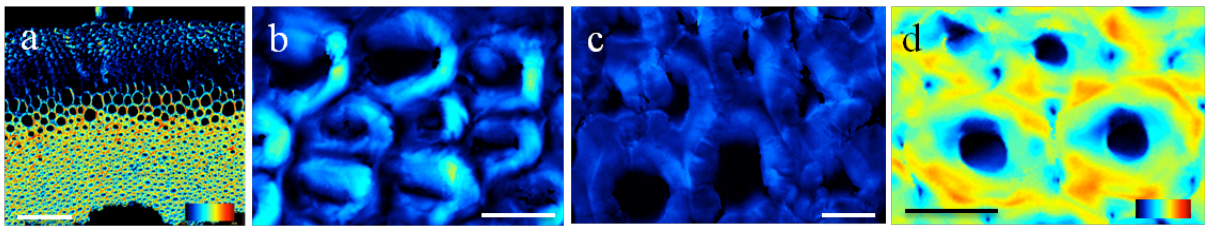

Fig. 2: (a) LC-PolScope retardance images of 10μm cross section of *Erodium gruinum*. (Scale: 100 μm, Retardance range: 27.3-259 nm). A close up of the different layers of the awn: (b) upper layer (c) middle layer (d) lower layer (Scale: 10 μm, Retardance range: 0-273 nm).

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IN-SITU X-RAY DIFFRACTION EXPERIMENTS OF AMYLOIDIC SYSTEMS ON LOTUS-LEAVES-LIKE ARTIFICIAL SUPERHYDROPHOBIC SURFACES

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The flows generated inside evaporating drops on superhydrophobic surfaces [1,2] (SHSs) mimicking the natural roughness of lotus leaves can fruitfully be exploited for manipulating matter at interfaces. Different kinds of poly(methyl methacrylate) (PMMA) SHSs have been designed and fabricated through the use of optical lithography and plasma processes (Figure 1, left). Aggregation into a fibrillar morphology with cross-β amyloidic structure has been observed by X-ray microdiffraction for small, natural peptides at the rim of drop-residues [3]. Such kind of studies are quite significant if one thinks about the involvement of amyloid fiber aggregates with many fatal neurodegenerative diseases such as Alzheimer's, Parkinson, the prion-related diseases, and non-neurodegenerative disorders such as type II diabetes. In particular, X-ray fiber diffraction analysis confirmed the concentration dependent conformational changes of the peptides in water (Fig. 1, right). These observations suggest that convective flow fields could be systematically explored for manipulating and probing of biopolymers such as proteins at interfaces.
Another subject which has been analyzed during the evaporation on superhydrophobic surfaces was lysozyme [4]. In order to promote lysozyme β-conversion we added Ca^{2+} ions which play a role in the β-conversion into amyloid β-peptide and silk-fibroin. The observed fiber texture and correspond to a fibrillar lysozyme phase. The transformation of lysozyme solution into a fibrillar amyloidic deposit with a cross-β structure occurs under conditions of weak acidity and high Ca^{2+} ionic strength, on a time scale much shorter (around 1 hour) than that reported in literature. In future experiments one could explore factors influencing different types of amyloidal deposits in a systematic way and model shear flow in evaporating drops.
The combination of drop deposition on superhydrophobic surfaces with SAXS/WAXS (Small and Wide Angle X-Ray Scattering) raster-scans by high brilliance X-ray microbeams will allow extending high-throughput probing of biomaterials [5] and proteins deposited to volumes which are orders of magnitudes smaller than currently probed.

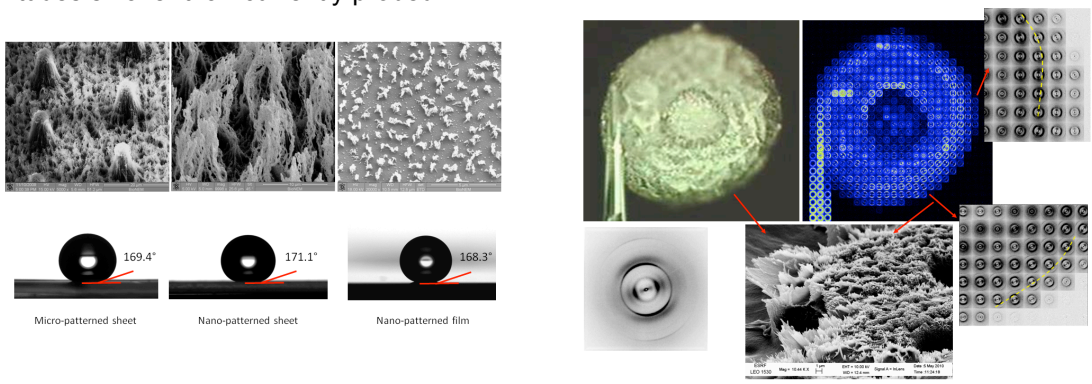

Fig. 1: Different kinds of PMMA superhydrophobic surfaces (SHS) mimicking *Nelumbo Nucifera* lotus leaves microstructures and relative contact angles (left); Optical, X-ray diffraction and SEM images of peptide amyloidic systems dried on PMMA-SHSs (right).

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A DESCRIPTION OF HAIRY, ORNAMENTED AND GLABROUS CRAB SHELLS (BRACHYURA) WITH A DISCUSSION OF THEIR BIOMIMETIC POSSIBILITIES

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Bacteria, diatoms and fungi have been founded as the most common microepibionts on crab carapaces, while protozoans and macroorganisms were the less common. Although some crab species could be heavily fouled, most of them show little or no fouling, even when compared with other living substrates, natural and artificial surfaces, crabs carapaces are the less fouled surface [1,2]. In this work we describe the microstructures (spines and/or seta), their distribution and sizes, founded at fragments of carapace of three different types of crab surfaces: hairy, ornamented and glabrous (some samples Fig.1), in order to design a crab carapace model. The crab carapaces are normally covered by two structures with different developmental grades depending the habitat and organism evolutive traits. The first one is a calcareous protuberance from the most external layer of the carapace (epicuticule), which could be described as a tubercle when is rather flat and wide and as spine when it is taller than wider. The second structure is a protein structure coming from the most internal layer of the carapace (dermis) and typically has live cell associated, this structure is described as setae (hair) and could be as simple as a stem or as complex as a multibranched structure. The ecological, behavioural and adaptative advantages of the variation found are discussed in the context of organism habitat and behaviour.

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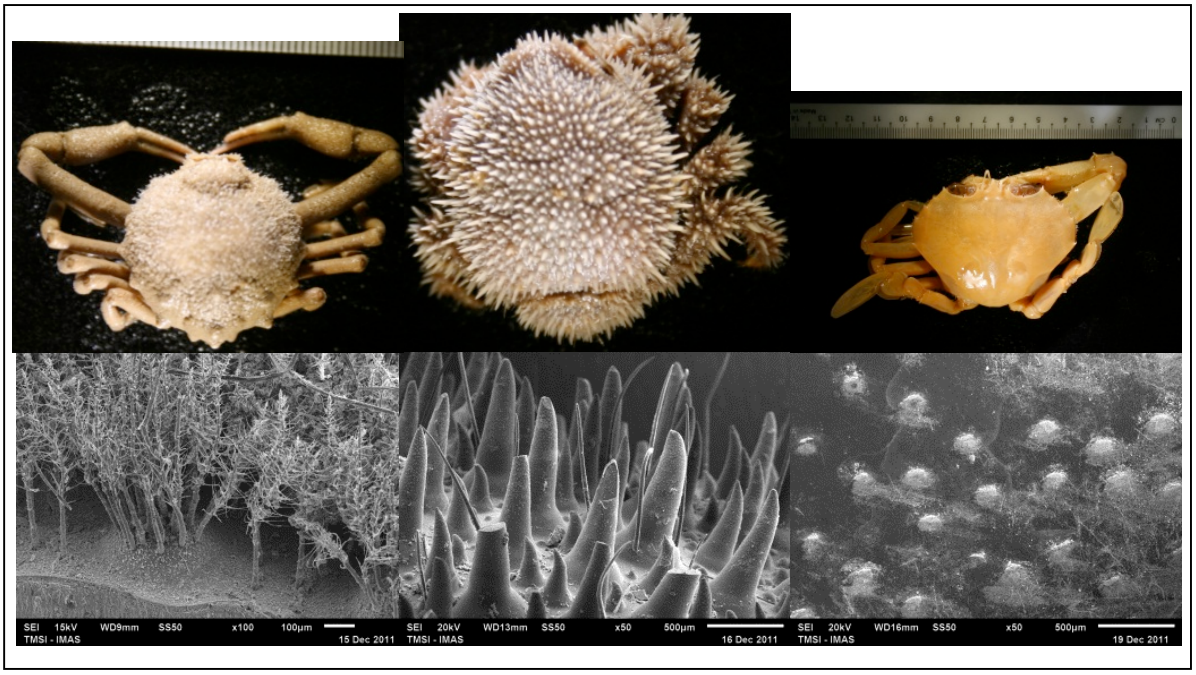

Fig. 1: Left column *Pariphiculus coronatus* (Alcock & Anderson, 1894); middle column *Acanthodromia margarita* (Alcock, 1899); right column *Ovalipes iridescens* (Miers, 1886). Upper row complete crab images, lower row SEM images.

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BIOINSPIRATION IN THE FIELD OF SELF-HEALING MATERIALS

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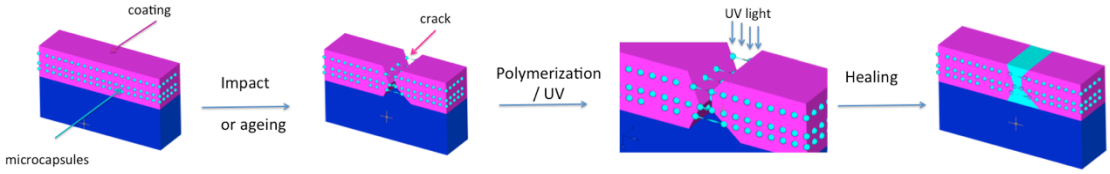
Inspired by nature, there is an innovative family of materials with self healing properties which has applications in many situations. This family of materials has been studied by many scientists since the publication of a notable paper about self-healing composites written by Professor S.R. White *et al*. in *Nature* in 2001.

The synthesis of self-healing materials can be acheived through three main routes. The first [1-2] involves encapsulating a monomer, the diclycopentadiene, which in the presence of Grubbs' catalyst (encapsulated or not), leads to a polymerization that fills cracks if the capsule is broken. The second route [3-4] involves preparing a material with hollow fibres containing a polymerizable formulation working like the veins in a living organism. The third route [5] uses supramolecular chemistry to recreate chemical bonds which have been broken.

The original direction we have chosen is to use environmental factors like exposure to air, humidity or light to trigger the polymerisation of encapsulated monomers and repair cracks in the materials they have been applied to. We will show in detail how this self-healing works and provide some examples of industrial applications.



Here we design and synthesize molecules that associate together to form both chains and cross-links via hydrogen bonds.

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SELF-HEALING POLYMERS BASED ON SOL-GEL CHEMISTRY

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The need for high-value materials with improved reliability has boosted research in a new class of materials namely self-healing materials. Self-healing materials are materials with the implemented capability of restoring either fully or partially any functionality lost due to cracks or scratches [1]. Self-healing systems can be classified into two main groups, (i) extrinsic, such as container-based systems in which the healing agent is added as a separate phase to matrix, and (ii) intrinsic, such as ionomers in which the polymer itself has a latent self-healing functionality due to the architecture of its molecules.

Sol-gel based polymers [2] are increasingly being used as surface pretreatments aiming at improving adhesion and barrier protection of metallic substrates, and/or to restore the chemical protection of the substrate by controlled release of corrosion inhibitors, the later being described as an extrinsic self-healing route [3]. However current sol-gel based coatings are not capable of closing (healing) scratches or healing cracks.

In this work we aim at development of intrinsic self-healing sol-gel based polymers which can repair themselves by closing possible defects occurring during service lifetime. Our current approach to address the problem is based on the incorporation of sulfur chemistry into hybrid sol-gel systems.

The newly developed polymers have been fully characterised (e.g. thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)) and their cohesive and adhesive healing capabilities have been analysed. In order to study cohesive healing of the new coatings, casted free films were cut using a razor blade and their healing behavior was monitored over time using optical microscopy. The adhesive healing of the hybrid systems was characterized using sequential shear failure and healing cycles. The results obtained are highly promising for the development of the first generation of self-healing sol-gel based coatings.

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EXTREME WETTABILITY AND TUNABLE ADHESION: BIOMIMICKING BEYOND NATURE?

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Nature has provided us luxuriant surface and interface resource pools with diverse wettabilities from superhydrophilicity to superhydrophobicity (two extremes) such as plant leaves (most typically the lotus leaves), feathers of birds, legs/back/wings of insects and silk of spiders. These parts of bodies possess properties of self-cleaning by minimizing the water and contaminant adhesion, or pinning spherical water droplet, collecting water droplet by integrating water vapor collection and droplet transportation. Surfaces with superhydrophobicity are usually fabricated by first forming hierarchical micro/nanoscale binary structures and afterwards chemical modification with low surface energy materials. The apparent surface wettability existing in nature can be simply mimicked by following the principle. With the expanded use of different coating materials, in particular, those smart materials in response to photo, thermal, pH, electro potential, electrolytes etc, some surface properties not observed in nature can be achieved, for instance, the switchable wettability that surface behave (super)hydrophobic under some circumstances and (super)hydrophilic in other cases, switchable water droplet adhesion between superhydrophobic pining state and superhydrophobic rolling state, superoleophobicity at the air/solid interface or even under vacuum, and self-healing wettability. “Inspired by nature, but achieving surface properties that nature doesn’t have”, we just call this as “biomimicing beyond nature”. This presentation firstly mentions about typical nature’s examples and the brief progress on biomimicing, turns to a detailed presentation of “biomimicing beyond nature” in the following four aspects: smart surfaces with reversibly switchable wettability, smart surfaces with reversibly switchable liquid droplet adhesion, superoleophobicity in air and under vacuum and self-healing superamphiphobicity. Finally some perspectives on future development are discussed.
People will continue to work on design and fabrication of surfaces with much faster and smarter responsive property and realize the real in-situ switch of wetting and adhesion. The new progress towards self-healing design will afford surfaces with mechanical robustness, abrasion and contamination resistant and durability etc, and thus surfaces with self-repairable characters would be a promising research direction in the area for the sake of the real applications in micro-fluidics, micro-reactors, oil transportation and automotive and aerospace devices.

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STRONG DRY ADHESIVES VIA BUCKLING-BASED INTERLOCKING

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Burdock seeds easily attach to animal furs via mechanical interlocking for reproduction purpose and can be easily removed by peeling. This interesting phenomenon has led to the invention of Velcro® tape. Here we applied this concept to micro-scale and demonstrate strong dry adhesion between epoxy-based shape memory polymer (SMP) pillar arrays in hexagonal array (1 μm in diameter, 4 μm in height, 2-3 μm in pitch). Shape memory polymer can be deformed to a temporary shape when heated above the phase transition temperature, where the bulk modulus of SMP drops 2-3 orders. Upon reheating, the original shape can be recovered, if the polymer is not permanent deformed, driven by entropic elasticity. In our system, the SMP pillars were heated to 80 ^{o}C, above the *T*g of SMP, where the Young's modulus dropped from 2.5 GPa (glassy state) to 3 MPa (rubbery state). Then a preload was applied to buckle the pillars. When brought into contact under the load, the buckled pillars became interweaved or indented with each other, forming micro-scale hooks and loops. The deformed structure was locked after cooling to room temperature, leading to strong adhesive force, up to ~53±25 N/cm^2 in the normal direction and ~72±23 N/cm^2 in the shear direction for pillars with an aspect ratio (=height/diameter) of 4. When separated at 80 ^{o}C, however, the adhesion between two SMP pillars was greatly reduced to ~3±2 N/cm^2 for normal load and ~7±1 N/cm^2 for shear load, respectively. This dramatic reduction in adhesion can be explained by the significantly decreased modulus of SMP above *T*g, thus, much less elastic energy stored in the pillars for separation. The coupling of mechanical deformation of SMP micropillars with modulus change demonstrated here could offer new insights to design superstrong yet reversible dry adhesives.

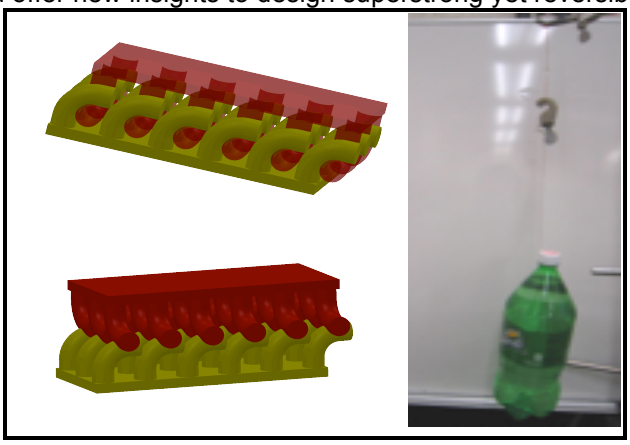

Fig. 1: Interlocking adhesion between two sets of buckled micropillar arrays

SIZE DEPENDENCE STUDY ON THE SUPERHYDROPHOBICITY FROM RASPBERRY-LIKE SILICA PARTICLES

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Over the last decade, superhydrophobic surfaces have attracted much interest for both fundamental research and practical application, mostly driven by the promise of self-cleaning properties of these coatings [1]. Mother Nature has delivered its secrets and research has revealed that the self-cleaning property originates from a peculiar topology based on micro- and nanoscopic surface roughness combined with the hydrophobic properties of its epicuticular wax [2].
For synthetic coatings, a dual-size roughness combined with low surface energy species appears to be essential to reach superhydrophobicity. In a previous cooperation between DSM and TU/e, a nature-inspired approach – christened the 'raspberry' approach – has been scientifically developed, leading to man-made superhydrophobic surfaces [3]. In this method, the key to introducing well-controlled dual-size (70/700 nm) roughness involved the synthesis of raspberry-like silica particles. Nowadays, superhydrophobicity is not sufficient for practical applications, and the trend is now driving research to the development of multifunctional coatings. Therefore, tuning the size of the raspberry-like particles to appropriate dimensions would lead to new applications.
The morphology of the raspberry-like particles is a key issue for the surface roughness of the film. The small particles synthesized by the well-known Stöber method appeared not to be suited to build-up the raspberry morphology. Basic amino acids were investigated as catalyst [4] for the hydrolysis-condensation of tetraethyl orthosilicate (TEOS), and led to the synthesis of well-defined raspberry-like particles within the targeted range.
Herein, we study the dependence of superhydrophobic properties on films originated from different sizes ratio of well-defined raspberry-like silica particles. The film shows an advancing contact angle of 163° and a roll-off angle of 1° (Fig. 1). The two synthetic approaches, using either ammonia or lysine as catalyst, are also compared. The synthesized particles were characterized by solid-state NMR and their morphology was evaluated by SEM and Cryo-TEM.

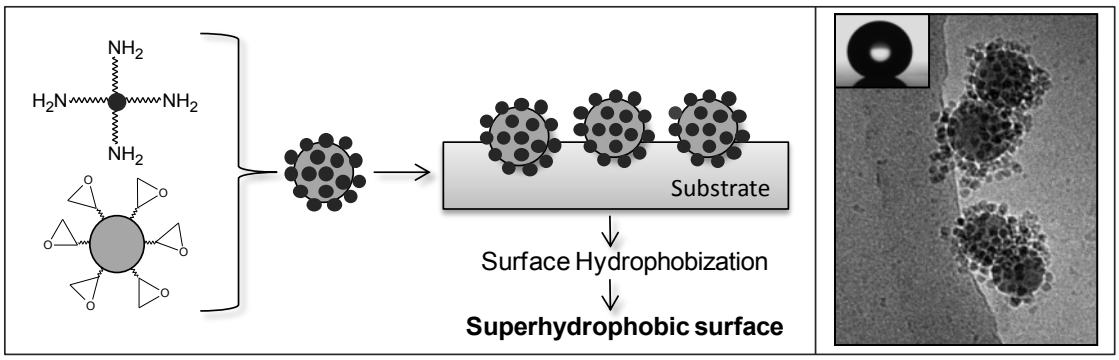

Fig. 1: Preparation of superhydrophobic films from raspberry-like silica particles (left) and Cryo-TEM images of raspberry-like particles. Inset: static water contact angle of a film made from the raspberry-like particles.

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SELF-ORGANIZED SUPRAMOLECULAR STRATEGY TOWARDS CONTROLLED SYNTHESIS OF NANO-STRUCTURED SILICA MATERIALS

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Silica-based materials are important for a wide range of technological applications, such as catalysts, polymeric fillers, coatings, chemical and biological separations, sensors, photonic and electronic devices, bio-encapsulation, enzyme immobilization, bioimaging, drug delivery, and so on. In nature, silica is widely appeared in the living things such as diatoms and sponges as cell walls and body spicles with precisely constructed hierarchical structures. In this sense, we think that in silica design, diatoms and sponges are eternal texts with a lot of sources of inspiration for the synthesis of silica-based nano/micro-scale materials. In the formation of biosilica, the specially structured organic matrices are indispensible which play as templates and catalysts for silica deposition. Therefore, in the biomimetic approach, we should focus our attention to the molecular regime by which we can control the silica with temporal and special fashion [1]. Our strategy for controlled synthesis of nano-structured silica materials including shaped powders and textured films is based on templated sol-gel reaction occurred on the suparamolecullar crystalline aggregates and layers that are self-organized from linear polyethyleneimine (LPEI) and small molecules (see Fig. 1). LPEI has very simple structure unit (-CH_2CH_2NH-) with secondary amine site in the main chain. We found that LPEI can adopt multiply shaped crystalline objects in aqueous media with association of water molecules or organic acidic compounds. The interest here is that the crystalline objects of LPEI played as catalysts and templates to promote rapidly the hydrolytic condensation of alkoxysilanes in aqueous media affording to nanowire, nanoribbon, nanotube, nanosheet based hierarchically structured silica. In this processing, a recipe for regulating an object of LPEI can result in the corresponding structured silica. Thus we can alter simply the silica morphology by changing the conditions of the LPEI organization. This is likely a programmed system where input of a chemical component for LPEI organization leads to output of a controlled silica. Such input/output relation is available not only for powders control but also for films alternation. Herein, it is worth to note that this program is easily productive of chiral nanosilica. A special chiral crystalline complex consisted of LPEI and D- or L-tartaric acid mediated chiral silica with positive or negative CD signs under neutral pH/ambient temperature. Very interestingly, the chiral silica obtained remained its CD activity even after sintered at 900°C. Employing the biomimetically nanostructured silica, we developed superhydrophobic device to control the liquid flow and dewetting, photocatalyst to decompose harmful gases and chemical pollution, photoluminescence for sensing, reactor for reducing metal ions and so on. We believe that our strategy for controlled synthesis of nanostructured silica materials will provide a generally acceptable method for designing silicon and metals related nanomaterials.

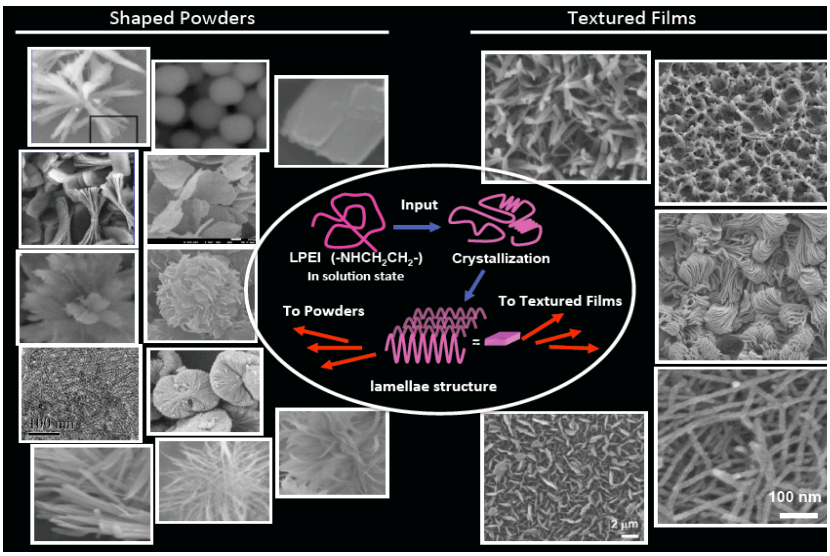

Fig. 1: Silica materials with powders and films fashions

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ICE TEMPLATING: A BIOINSPIRED PROCESSING ROUTE FOR POROUS MATERIALS

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The freezing of colloids is an amazingly common phenomenon encountered in many natural and engineering processes such as the freezing of soils, food engineering or cryobiology. It can also be used as a bioinspired, versatile and environmentally-friendly processing route for bioinspired porous materials and composites exhibiting breakthroughs in functional properties [1]. Yet, it is still a puzzling phenomenon with many unexplained features, due to the complexity of the system, the space and time scales at which the process should be investigated and the multidisciplinary approach required to completely apprehend it.
I will summarize our work to progress towards a deep understanding of ice templating and the freezing of colloids through novel in situ observations approaches [2-4], to exert a better control on the processing route [5,6] and achieve the full potential of this novel class of bioinspired materials.
Strategies borrowed from work in geophysics, cryobiology or colloidal self-assembly can provide innovative control of the freezing process and the derived structures and open new opportunities in these domains.

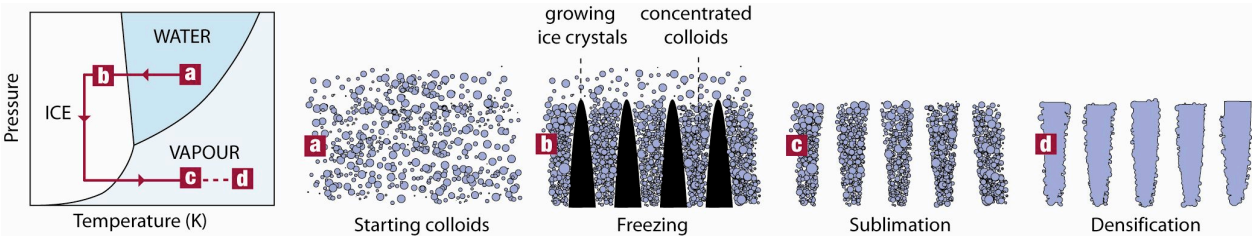

Fig. 1: Principles of ice templating.

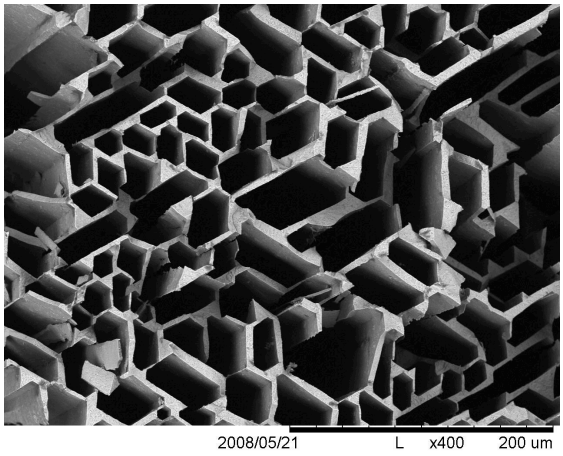

Fig. 2: Typical microstructure of an ice-templated porous ceramic, cross-section perpendicular to the freezing direction.

[1] S. Deville, E. Saiz, R. K. Nalla, A. P. Tomsia, *Science,* **2006**, 311, 515-518.
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SYNTHESIS OF HIERARCHICAL TiO_2 NANOSTRUCTURES USING COTTON AND FERULA AS A CHEMICAL REAGENT AND A TEMPLATE.

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Metal oxides are important functional materials with properties frequently related to the process used for the preparation. One of them is the replication of biological templates by deposition of an oxide layer using a sol-gel process: it is a promising strategy for the production of hierarchical oxide structures[1] and a wide variety of templates have been used, including cellulose [2].
In this idea, we propose a new approach for the synthesis of oxides with hierarchical structures, based on reaction of a metal chloride with a cellulosic natural material acting as both the oxygen-donor reagent and a template. Because cellulose is built of D-glucose monomers linked by β-1,4 ether linkages, it is an excellent oxygen source and both the hydroxyl and the ether groups can react with $TiCl_4$, leading to the formation of TiO_2 according to classical reactions in Non-hydrolytic Sol-Gel route [3].
This approach is thus completely different from the classical surface sol-gel approach in which the template is only a mould over which an oxide layer is deposited. Here, the organic template is gradually and partially replaced by the oxide phase, as in a mineralisation or fossilization process. To demonstrate the potentialities of this approach we report here the synthesis of nanostructured TiO_2 by reaction of $TiCl_4$ with cotton wool or with the pith of ferula communis [4].(Scheme 1).

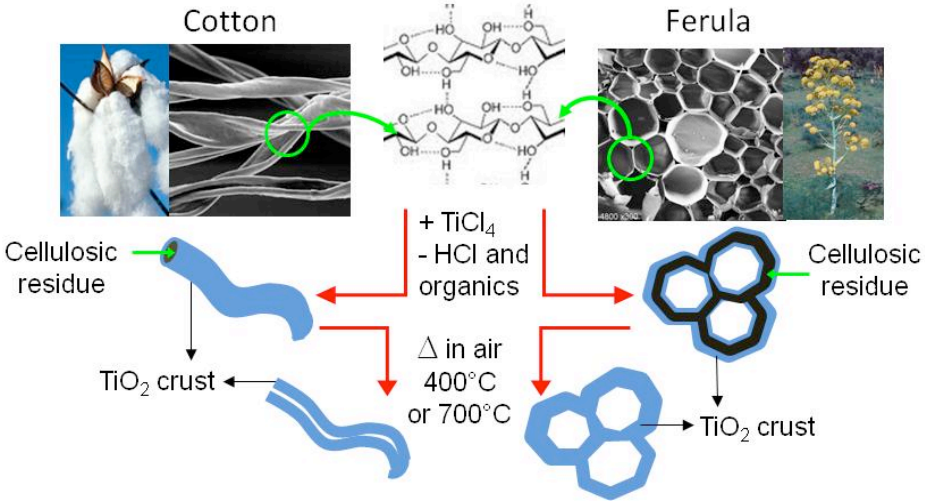

Fig. 1:General pathway for the preparation of TiO_2 micro- nano- structures by solid-liquid reaction between cotton fibers or ferula pith and $TiCl_4$ followed by calcination.

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BIOLOGICALLY INSPIRED PROCESSING OF METAL OXIDE MATERIALS

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Nature offers incredible examples of unique approaches to the challenges of the synthesis of nanoscale materials. Animals, plants, and microbes are the consummate material scientists. This is no more apparent than in those organisms that live in glasshouses; diatoms and sponges. Collectively, these organisms process gigatonnes of SiO_2 per year into intricate three-dimensional structures that fire the imagination. To obtain this exquisite level of molecular control, organisms often utilize a well-orchestrated process involving active supramolecular organization of biological templates that impart sensitive interfacial recognition of appropriate metal ions that are regulated through tightly controlled cellular processes. While the broad brushstrokes of biosilica formation are just beginning to be understood, far less attention has been paid to the biologically controlled disassembly of silica. Further, how each of the components of this complex systém work in concert is not well understood. In this presentation, we will outline new chemical biology approaches for the study of silica processing within these organisms. Additionally, we will examine biomimetic approaches to the design and synthesis of enzymes and small molecules capable of metal oxide synthesis and degradation. The resulting system represents a new enzyme based lithography.

SYNTHESIS OF HOLLOW SILICA PARTICLES VIA A BIOSILIFICATION LIKE ETCHING PROCESS

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The synthesis of hollow silica particles has attracted widespread attention in recent years due to their unique properties and numerous applications in the fields of catalysis, separation, cell-labeling, ultrasound imaging, photonic crystals, and drug delivery. In this abstract, We report here fabrication of hollow silica particles via a biosilification like etching process. Different from the conventional template method, the new method uses the silica particles as starting materials which were synthesized using the well-known Stöber method. In the hollow silica preparation, first, we gently etch the silica particles with a NaOH solution without using template molecules to make them porous. Then we coat the porous silica particles with poly-dimethyldiallylammonium chloride (PDDA) and treat the PDDA-coated porous silica with an ammonia solution. the hollow silica microcapsules could be obtained as a result of the interaction between the anionic silicate oligomers and the cationic polyelectrolyte shell. Such a process is similar to the natural biosilification process in most of the diatom cells in which the biomolecules capture the silicate species from the aqueous environment through organic-inorganic interactions and direct the formation of various morphologies. In this study, we found that the NaOH dosage and ammonia concentration have significant impact on the morphology of the final products. The as-prepared hollow silica particles have mesopores larger than 10 nm on their wall, which show potential application in immobilizing biomolecules.

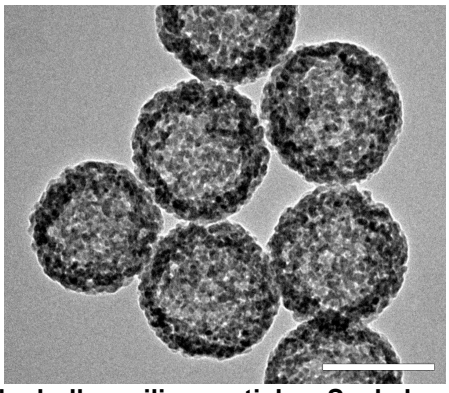

Fig. 1: TEM of the hollow silica particles. Scale bar is 200 nm.

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CELLULOSE NANOCRYSTAL REINFORCED HIGHLY ELASTIC RUBBER COMPOSITES

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Cellulose nanocrystals (CNCs) have recently attracted interest in nanocomposite research because of their exceptional mechanical properties, availability and sustainability. Still, their hydrophilic nature has hindered their use as reinforcing agents with hydrophobic polymer matrices.
We describe the synthesis of highly hydrophobic, crosslinkable CNCs of cotton origin and their use in polybutadiene rubber composites. Composite films were prepared with up to 80% weight fraction of the modified CNCs and crosslinked by a UV-initiated thiol-ene reaction. Transmission electron microscopy and atomic force microscopy of the films revealed partially oriented, intercalated regions of the modified CNCs and the polymer.
The modified CNCs had a significant reinforcing effect of over one order of magnitude on the ultimate tensile strength of the composites (Fig. 1a). The composite films show elastic behavior with excellent strains of break in the range of 15-75% (Fig. 1b). Remarkably, the hydrophobic nature of the composites manifests in that air humidity changes have no effect on the mechanical properties. These materials combine the elastic rubber and strong biobased CNCs in a unique way and could be used in applications where moisture insensitivity is indispensable.

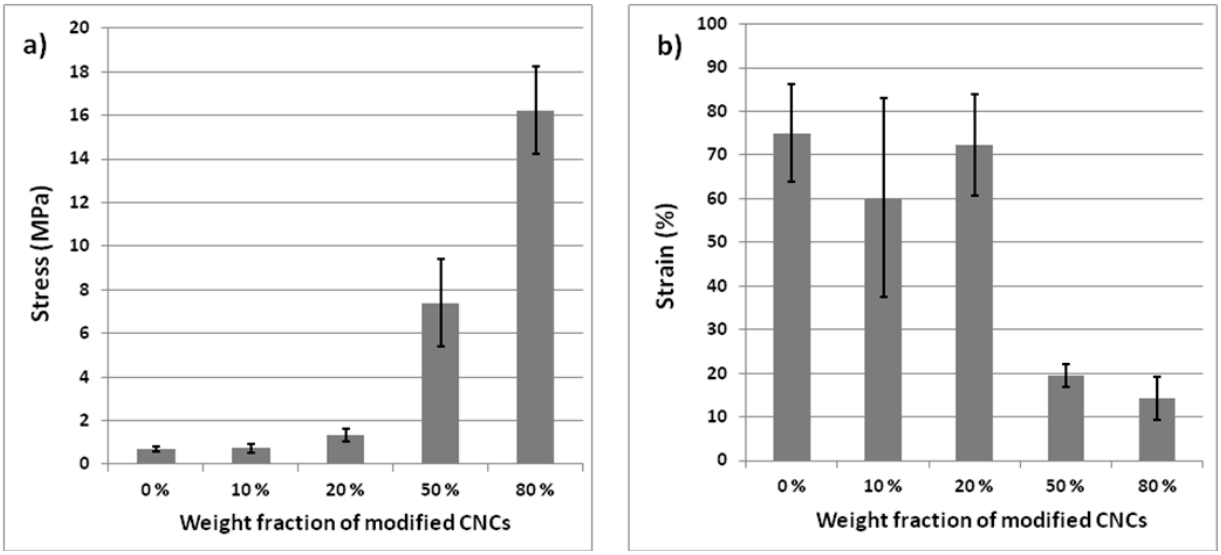

Fig. 1: Mechanical properties of the composite films, a) ultimate tensile strength, b) strain at break.

BIO-INSPIRED CHITIN-OXIDE NANOCOMPOSITES THROUGH SELF-ASSEMBLY

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[2]*Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Sofia, Bulgaria*

We develop and present a versatile colloid-based approach for the large-scale synthesis of a new family of hybrid bioorganic-inorganic nano-composites with an unprecedented control of the texture and morphology [1].
This approach combines the self-assembly properties of polysaccharide α-chitin nanorods (bundles of monocrystals (D = 3.2 ±0.6 nm) with amino groups at their surface) [2] with the flexibility of sol-gel processes involving siloxane oligomers (Fig. 1a, 1b). It has been developed through the formation and processing of stable suspensions containing the two colloids chitin nanorods and siloxane oligomers in a dispersed state. This is a challenging issue owing to differences in stability and reactivity of these colloids. Like for pure chitin nanorods suspensions, the chitin-siloxane co- suspensions undergo an isotropic to nematic transition when concentrated beyond ca. 2%. The ordered phase exhibits optical birefringence, and is highly responsive to the application of external fields (shearing, electric, magnetic).
The nano-composites obtained after concentrating the suspensions can be uniaxially oriented over millimeters by applying a strong (9.4 T) magnetic field during solvent evaporation across the sol- gel transition (Fig. 1c, 1d). Experiments are currently ongoing to determine more precisely the mechanisms at play in the self-assembly. Evidences suggesting the formation of chitin-silica hybrid colloids are being assessed by a combination of spectroscopic (NMR, XPS) and diffusion techniques (synchrotron-SAXS, light scattering). Besides, microparticles have been obtained using spray-drying processes, with mean diameters in the 2.3 micrometer range.
We also show that the characteristics of the silica-chitin nano-composites (morphology, texture, birefringence if any) can be transferred to their mesoporous counterpart by simple calcination [1,3]. Within the calcined materials, the pore diameters and specific surface areas are in the 4-8 nm and 0-450 m .g ranges respectively. For heterogeneous catalysis' applications (selective oxidation of alkanes), titatium alkoxides have been introduced in the synthesis' protocol in order to form mixed oxides SiO_2-TiO_2 (Ti/Si < 0.1). The dispersion of Ti sites can be tuned through synthesis conditions.
During our presentation, last results about chitin and silica colloidal self-assembly, materials' synthesis and characterisation, and catalytic applications will be given.

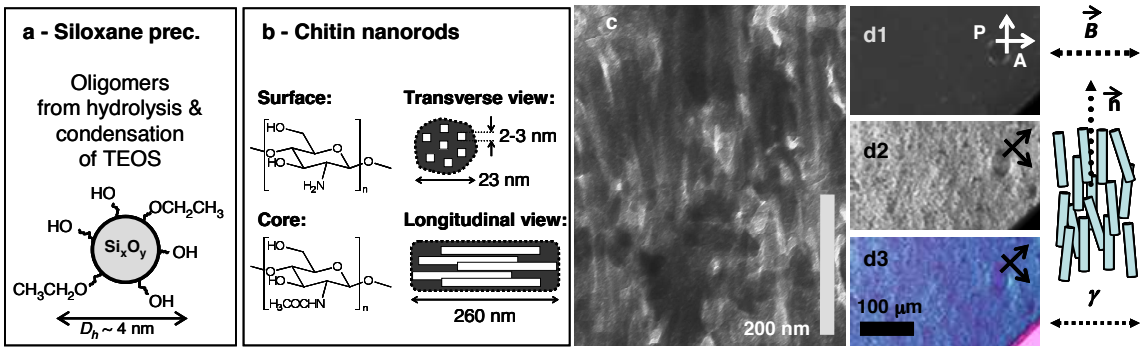

Fig. 1: Siloxane oligomers (a) and chitin nanorods (b) can be self-assembled into nano-composites possessing high textural ordering, especially when external fields are applied during processing (e.g. static magnetic field *B* in c, d).

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LIGHT TRIGGERED GELATION AND ADHESION BY USING CAGED MARINE ADHESIVE PROTEIN MIMETIC POLYMER

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The mussel adheres to various surfaces (even polyethylene or Teflon surface) in water by using marine adhesive protein (MAP). It is well known that mussel MAP specifically contains “non-standard” amino acid 3,4-dihydroxyphenyalanine, which works as a cross-linking point and interact with surface to give strong adhesion.[1] We already synthesized a water soluble poly(acrylamide) derivatives having dihydroxyphenyl groups and amino groups as a mussel MAP mimetic, and transformed to an adhesive hydrogel by aerobic oxidation. As a biomimetic approach, it is interesting to control function of the polymer by chemically modified catechol units. For this approach, we adopt “caged compounds”, which contain photocleavable-protecting groups. These compounds enable the activation of compounds to be controlled in time and space by light irradiation. We designed and synthesized caged MAP mimetic polymer which have *o*-nitrobenzyl protected catechol groups. It is expected that, caged MAP mimetics will be stable even under oxidative conditions, and can be activated at a suitable time and position by light irradiation (Fig. 1).

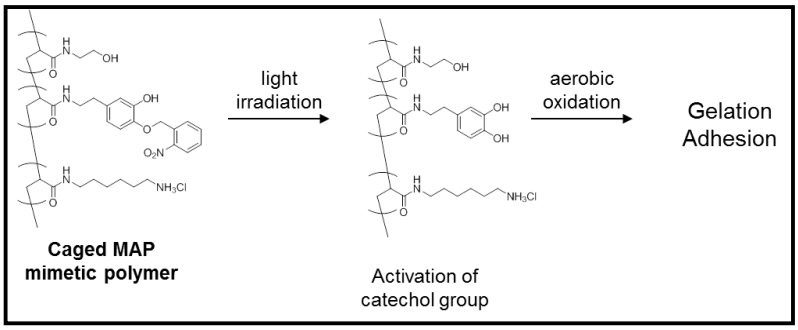

Fig 1: Light-activation of caged MAP mimetic polymer.

A phosphate buffer (0.1 mol/L, pH= 8.0) solution of the caged MAP mimetic polymer was irradiated with visible light for 30 min by using a mercury xenon lamp light source. UV component was filtered out by a glass plate placed between the lamp and solution. After irradiation, formation of gel was observed (Fig. 2a), whereas no gelation was observed without light irradiation (Fig. 2b). This result clearly indicates that the protecting group on catechol was removed by light irradiation to induce subsequent oxidation reaction with molecular oxygen forming cross-linking structure.

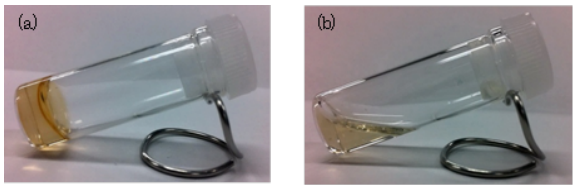

Fig. 2: Caged MAP mimetic polymer in phosphate buffer solution (a) after light irradiation for 30 min and (b) without light irradiation.

The caged MAP mimetic polymer solution was put on a glass plate, and sandwiched between two glass plates. The sample was fixed by clamps, and light was irradiated in air. Then, the sample was stored in a humid atmosphere at room temperature for 24 h to allow the oxidation reaction to proceed. The two substrates adhered through gelation of the polymer solution. The sample was set on a tensile tester and the lap shear adhesion strength was measured. The glass plates adhered by caged MAP mimetic polymer broke at a lap shear adhesion strength of 0.061 ± 0.006 MPa. Broken hydrogel remained on the failed area of each glass plate surface, indicating that cohesive failure took place at the polymer gel. Since MAP mimetic polymer interacted so strongly with the glass surface, fracture occurred inside the hydrogel layer.

We constructed a novel light-controllable functional MAP mimetic polymer by combining an artificial photolabile protection technique and naturally inspired catechol chemistry. The synthesized polymer was stable even in the oxidative condition, in which free catechol resulted in self-reacted oligomers through oxidation. On the other hand, the polymer was activated by light irradiation, and gel formation and adhesion of glass plates were achieved from an aqueous solution of the polymer.

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VARIOUS CONTROLLED ZNO MICRO- AND NANO-STRUCTURES: MORPHOLOGIESCONTROLLED, WETTABILITIES AND MECHANICAL PROPERTIES

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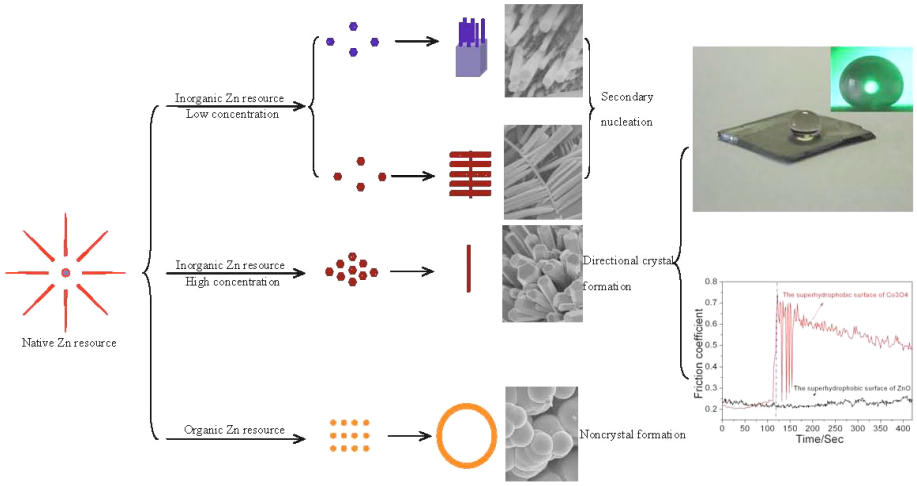
ZnO nanomaterials is a promising semiconductor with a wide band gap (Eg=3.37 eV). Here we report the synthesis of various ZnO micro-and nanostructures on silicon wafers by a low-temperature, environmentally benign, solution-based route. The size, shape, and density of the ZnO structures were well-controlled by appropriately tuning the growth conditions. We found that the complex ZnO nanostructures are obtained when the concentrations of the inorganic Zn resources are low, which should be attributed to the secondary nucleation growth due the line defect. The hexagonal ZnO micro-rods can be observed when the concentrations of the inorganic Zn resources are high, and the formation mechanism should be an epitaxial growth. When the Zn resource is organic compound, the ZnO hollow nano- and micro-spheres are formed. We also discussed the wettabilities of the resulting surfaces with various ZnO structures, finding that the surfaces show superhydrophilic and superhydrophobic before and after chemical modification, respectively. Finally, we evaluated the surface mechanical properties for the surface only constituted by hexagonal ZnO micro-rods by a tribological tester, showing the surface is more robust than that of the binary structure superhydrophobic surface.



ANISOTROPIC WETTING ON DIRECTIONAL GOLD NANOWIRES

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Lessons from nature may provide us important inspiration to develop new methods and approaches for fabrication of novel synthetic functional materials. One of the convenient inspirations from living creatures is the wetting behavior of surfaces which may have a wide variety of practical applications in daily life and industry. Here, we present an engineered nanofilm, composed of an array of directional gold nanorods, which demonstrates distinct static contact angles depending on both surface morphology and chemistry (Fig. 1). Nanofilm morphology could be adjusted conveniently in desired range by holding the substrate with a constant glancing angle to the incoming vapor flux. Furthermore, the nanoscale structured surfaces were modified with thiol molecules having different end groups to understand the influence of surface chemistry on anisotropic wetting. It was found that surface micro/ nanostructure morphology and chemistry are extremely important for the manipulation of water droplet on the directional surfaces.

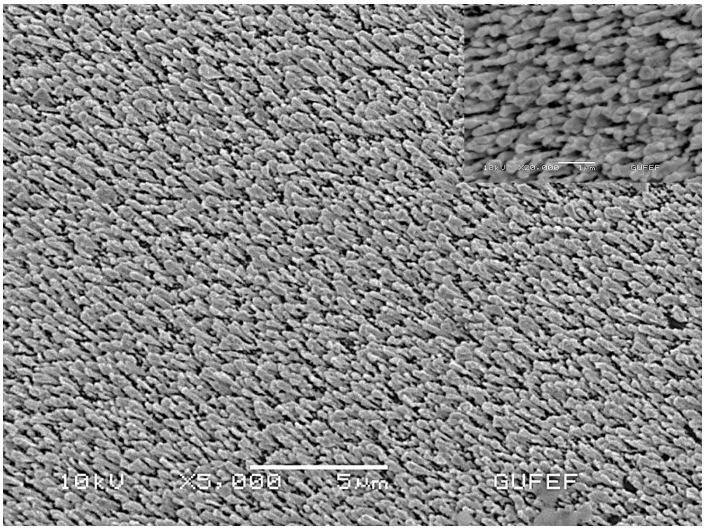

Fig. 1: SEM images of directional gold nanowires

SELF-HEALING THERMAL CONDUCTIVE ADHESIVES

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Materials presenting self-healing or self-repairing properties have now been a reality for over a decade. This new field of material has already been successfully applied in many domains from aerospace to civil engineering. By mimicking what living organisms do, it is now possible to produce concrete, asphalts, ceramics, coatings and polymer composite presenting self-healing properties.
In this work we focus on the development of a thermally triggered self-healing composite to create multifunctional materials presenting 3 self-healing properties: cohesion, adhesion and thermal/electrical conduction. In the composite, the self-healing properties are carried by the polymeric matrix which is based on a polysulfide rubber thermoset. The presence of disulphides bonds in the polymeric network gives to this thermoset network a thermally triggered dynamic bonding ability [1]. The density of the produce polymeric network as well as the polymeric chain composition (containing aliphatic or aromatic functions) has shown to have a significant effect on the cohesive and adhesive self-healing response of the material [2].

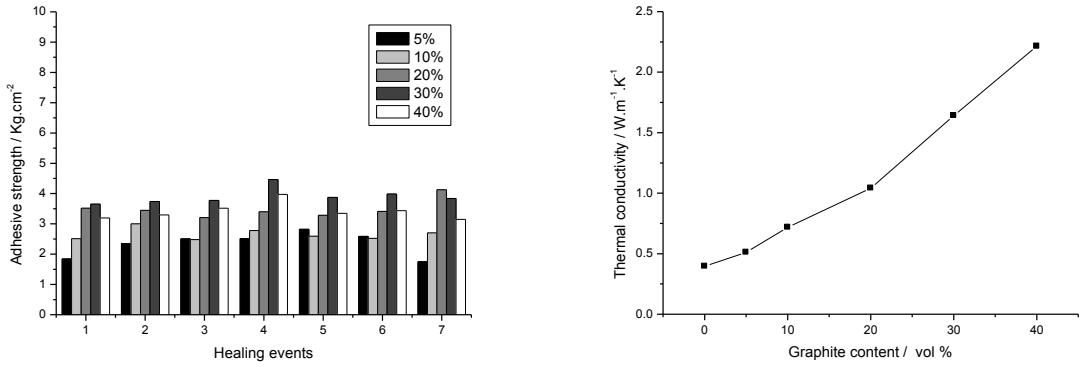

Fig. 1: Adhesion recovery (a) and thermal conduction (b) as function of the filler content

We create several type of composite using either an aromatic or an aliphatic based polymeric network filled with graphite or hexagonal BN particles. The effect of the charge loading on the material cohesive, adhesive and thermal conductive functionalities has been investigated and will be presented as function of the healing and the filler contents. This new class of material could have a positive impact on the reliability of (opto)electronic devices [3].

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POLYPEPTIDE–POLYSTYRENE MIKTOARM STAR COPOLYMERS: CONTROL OF SELF-ASSEMBLY BY POLYPEPTIDE ARMS

Susanna Junnila,[1] Nikolay Houbenov,[1] Anastasis Karatzas,[2] Nikos Hadjichristidis,[2,3] Akira Hirao,[4] Hermis Iatrou,*[,2] Olli Ikkala*[,1]

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Polypeptide blocks can adopt different protein-like conformations, such as α-helices and β-sheets, even when part of a block copolymer with conventional synthetic coil-like chains. We have employed different polypeptide blocks in nonlinear block copolymer architectures, namely in miktoarm star copolymers (see Fig. 1), where multiple blocks are connected in a single branching point [1].
These A_2B and A_2B_2 type miktoarm star copolymers are composed of polystyrene (PS) and three different polypeptide-based arms: (i) poly(*ε-tert*-butyloxycarbonyl-L-lysine), PBLL; (ii) poly(L-lysine hydrochloride), PLLHCl; and (iii) the supramolecular ionic complex of PLLHCl and sodium dodecyl sulfonate (DS), PLL(DS). The self-assemblies of these six miktoarm star copolymers are studied in the bulk solid state by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR) and small- and wide-angle X-ray scattering (SAXS, WAXS).
We have observed that the self-assemblies can be effectively controlled by the choice of the polypeptide side chain: the α-helical conformation in PS_2PBLL and PS_2PBLL_2 miktoarms promotes lamellar self-assemblies (Fig. 1a), while the random conformations in $PS_2PLLHCl$ and $PS_2PLLHCl_2$ are observed to cluster together, forming polypeptide micelles in a PS matrix (Fig. 1b). Ionic complexation of the polypeptide arms in $PS_2PLL(DS)$ and $PS_2(PLL(DS))_2$ leads to small-scale lamellar self-assemblies originating from alternating polypeptide and surfactant layers (Fig. 1c).

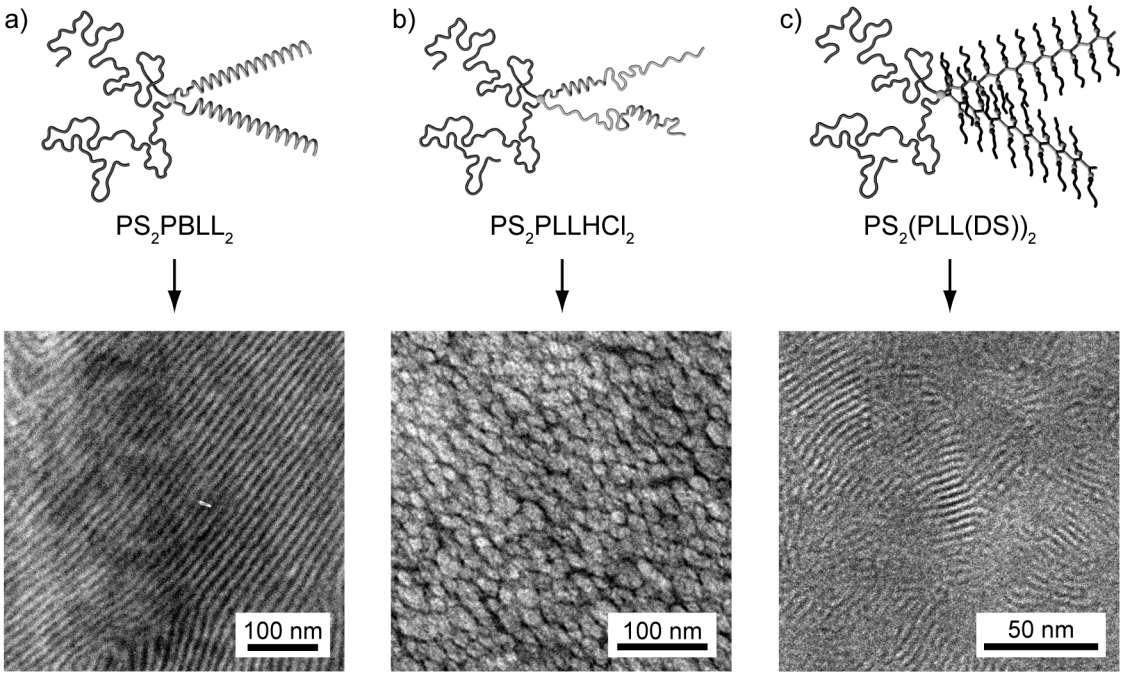

Fig. 1: Molecular architectures and TEM micrographs of the A_2B_2 type miktoarm star copolymers stained with RuO_4 (PS dark).

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DEVELOPMENT OF CHITOSAN BASED MICROCAPSULES BY ELECTROSTATIC LAYER BY LAYER METHOD TO ENCAPSULATE LIGNANS FOR TEXTILE APPLICATIONS

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The research project involves the development of biomaterials based microcapsules to encapsulate natural products like lignans with defined release kinetics and controlled release mechanism, and the grafting of the encapsulated lignans to the textiles is done in order to attain functionalities after integrating into the garments. Lignans have beneficial effect to the flora on the skins and scalable control over the skin moisture content, and the encapsulated lignans in the functionalized textiles provide better interaction with the skins in terms of reducing bacterial and/or fungal activities. The intelligent integration of functionalized textiles into the garments especially aims at integration of the materials on some areas of the garments which could provide high protection and comfort on contact with skin during some specific physiological activities.

In the present study, the microcapsules with an oil core and multilayer shell structure are developed from poly-cationic bio-based material chitosan (CS) and anionic surfactant sodium dodecyl sulfate (SDS) in multi-step electrostatic layer by layer deposition technique combined with oil in water emulsification process as shown in Fig. 1. The alkali treatment of the microcapsules with few drops of butanol is performed at the end to solidify the outer shell of microcapsules. The microcapsules formed by this technique show positive charge on the surface and controlled alkali treatment of microcapsules causes charge neutralization of microcapsules to provide better functionalities of encapsulated lignans in textiles. The diameter of the microcapsules varies from 2-10 µm with average diameter of 4.0 µm, and average diameter of the microcapsules increases after alkali treatment suggesting some aggregate formation by the microcapsules, which is the major problem during the preparation of concentrated microcapsule suspension as confirmed in optical microscopy and scanning electron microscopy. The optimization of microcapsulation process is currently being performed for the better functionalities of the textiles in the garments and the optimization step involves the use of different materials like bi-anionic surfactant instead of SDS and/or arabic gum, alginate, or simple sodium sulfate salt to ensure maximum deposition on materials on shell structure of microcapsules.

Functionalized textiles should be intelligently integrated into the garments. Thus, a specific and an accurate design of the garment based on advanced 3D design technologies are required. This enables a precise identification of interaction areas with the skin to increase the effectiveness of the expected properties: the functionalized areas should be placed in the right place and the garment should allow interaction with the skin during the practice of the considered activities.

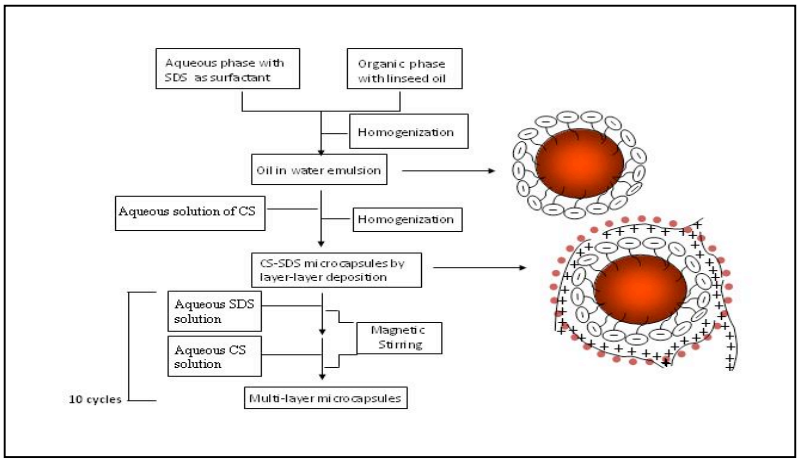

Fig. 1: Schematic diagram of microcapsule formation by electrostatic layer by layer deposition

BIOCOMPATIBLE SILICA NANOMATERIALS GRAFTED AMPHIPHILIC BLOCK COPOLYMER AND CONJUGATED WITH INDOCYANINE GREEN

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[4]*University of Basel*, Basel, Switzerland

The objective of this study is to develop a nanocomposites system for stabilisation of indocyanine green (ICG) in aqueous media to be used in medical application. The first obtained result was the understanding of the necessity to encapsulate ICG in a hydrophobic environment; this media improve considerably the stability of ICG. For this reason, the choice of polymer depends on three crucial properties: hydrophobic, biocompatible and biodegradable. Accordingly, Poly(ε-Caprolactone) has been chosen for the encapsulation of ICG.
Starting from a well defined silica core of approx. 80 nm, acting as template for a "grafting from" approach of Poly(ε-Caprolactone), ICG was embedded into the hydrophobic polymer coating. To enhance the hydrophilicity of the nanoparticles surface with a respect to necessity of the hydrophobic environment, the anionic coordinated polymerisation of L-Lactide was initiated from the hydroxyl groups of the Poly(ε-Caprolactone). The encapsulation of the Si@PCl/ICG with Poly(L-Lactide) improved considerably the colloidal stability of the nanoparticles. The obtained nanocomposites were based on silica nanoparticles grafted with diblock copolymer "PCl-b-PLLA" and embedded with ICG. It was characterised by IR spectroscopy, TGA, DSC and SEM. The block copolymer was studied with NMR and SEC. The colloidal stability of the nanoparticles was followed by zeta potential.
The approach to synthesize nanocomposites based ICG demonstrates a new route to stabilise ICG. We obtained biocompatible nanoparticles containing a high ICG concentration; exhibit an excellent stability against photo degradation and aqueous decomposition.

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THE INFLUENCE OF POLYMERS ON GROWTH OF BIOGENIC CRYSTALS IN AQUEOUS SOLUTION AND ON SOLID SURFACES

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Interactions of polymers with growing crystals, with polymers acting either as crystallization inhibitors or as templates, are at the roots of biological mineralization processes. Polymers are also used in the production of inorganic materials whenever precise control of crystal size, morphology and texture is required. In this paper, examples of polymer/crystal interactions (a) in aqueous solutions [1-3] and (b) upon/within polyelectrolyte multilayers deposited on solid surfaces [4] will be discussed. As model the *calcium phosphate crystallization system* will be presented.
Experimental methods: Imaging - SEM, EDX, CLSM and/or AFM; Crystal structure - XRD, ATR-FTIR
(a)*Polymer/crystal interactions in aqueous solutions* depend on the charge and secondary structure of the macromolecule. The underlying mechanisms are selective adsorption of the macromolecules either at specific crystal planes or - at the nucleation stage - at specific crystal polymorphs. Examples of specific changes in crystal growth morphology and of changes in the crystallizing polymorph resulting from such interactions will be shown. It will also be demonstrated that polymers, if added to a crystallization system, may have a dual role, i.e. depending on their concentration they may act either as promoters or inhibitors of crystallization.
(b) When polymers are adsorbed *at solid surfaces*, they may become templates for crystal nucleation. In our laboratory this possibility was used to prepare model organic-inorganic nano-composite coatings for artificial metal implants for bone and tooth replacement or repair. Glass and/or titanium plates were coated with polyelectrolyte multilayers: $(PLL/PGA)_n$, $(PLL/PAA)_n$ or $(PLL/CS)_n$, [where PLL is poly-L-lysine, PGA is poly-L-glutamate, PAA is poly-L-aspartate and CS is chondroitin sulfate] or mixed multilayers with a (PLL/PGA)n base and a $(PLL/PAA)_m$ or $(PLL/CS)_x$ top layer. The coated substrates were immersed into a metastable calcium phosphate solution for specified lengths of time. The resulting crystals (Fig. 1) were identified as calcium deficient apatite with platelet-like morphology and crystal sizes in the submicron range. On glass plates, crystals were relatively homogeneously spread; while on chemically etched titanium plates they followed the substrate topography as did the underlying polymer. Using ATR-FTIR spectroscopy, the nucleating efficiency of the polyanions in mixed multilayers was estimated as: PGA < CS < PAA. The differences are explained on the basis of surface structure and charge distribution of the polymer layers.

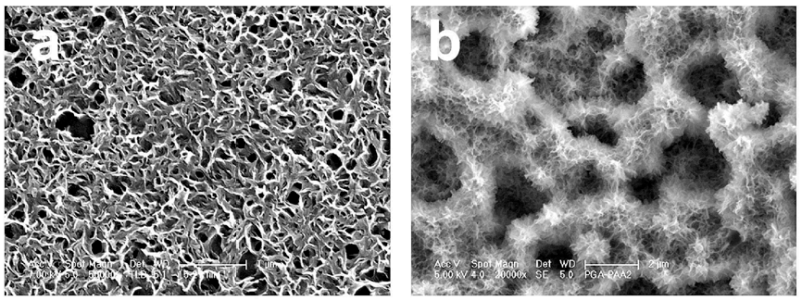

Fig.1: HRSEM micrographs of calcium phosphate crystals grown on: (a) glass plate coated with (PLL/PAA)6; magn. x 50 000; Ca/P = 1.50, (b) Ti plate coated with (PLL/PGA)20-(PLL/PAA)5, magn. x20 000; Ca/P = 1.52

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ARTIFICIAL BIOMINERAL FORMED BY INCORPORATION OF COPOLYMER MICELLES IN CALCITE CRYSTALS

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Advances in technology demand an ever-increasing degree of control over material structure, properties and function. As the properties of monolithic materials are necessary limited, one route to extending them is to create a composite by combining contrasting materials. Biominerals exhibit morphologies, hierarchical ordering and properties that invariably surpass those of their synthetic counterparts [1]. A key feature of these materials, which sets them apart from synthetic crystals, is their nano-composite structure, which derives from intimate association of organic molecules with the mineral host [2].

This study demonstrate the production of artificial biominerals where single crystals of calcite occlude a remarkable 13 wt% of 20 nm anionic diblock copolymer micelles, which act as 'pseudo-proteins'. This was achieved by a simple one-pot method, where calcium carbonate was precipitated in the presence of the micelles as soluble additives under ambient aqueous conditions [3]. A range of techniques including IR spectroscopy, high resolution powder XRD and high resolution TEM were used to compare the structures of these crystals with calcite single crystals of geological and biogenic origin. The synthetic crystals exhibit analogous texture and defect structures to biogenic calcite crystals and are harder than pure calcite.

This system provides a unique model for understanding biomineral formation, giving insight into both the mechanism of occlusion of biomacromolecules within single crystals, and the relationship between the macroscopic mechanical properties of a crystal and its microscopic structure. It is also envisaged that this versatile biomimetic strategy could be applied to many other crystalline systems, potentially leading to new materials with selected compositions and properties.

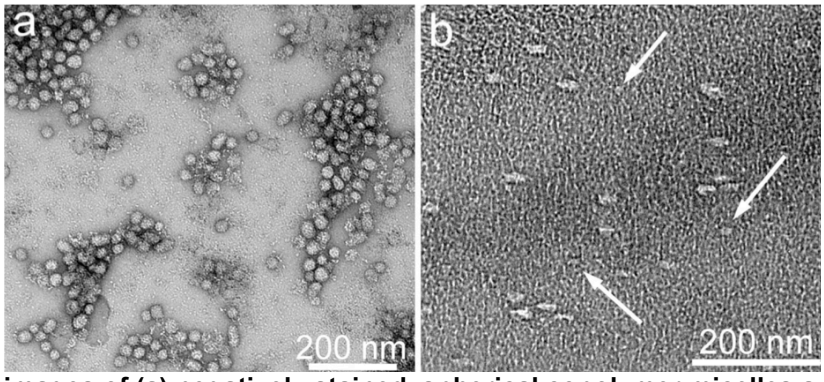

Fig. 1: TEM images of (a) negatively stained, spherical copolymer micelles and (b) a thin section cut through the nanocomposite crystal showing occluded copolymer micelles

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ADHESION STUDIES OF GASTROLITH COMPONENTS AND INTERACTIONS OF MODIFIED CELLULOSE FOR BIOCOMPOSITE FORMATION

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The adhesive properties of gastroliths of a fresh water crayfish (*Cherax quadricarinatus*) were quantified using colloidal probe atomic force microscopy [1]. Sequential detachment and large adhesion energies were observed between native gastrolith substrates and colloidal probes consisting of microparticles of heavily demineralized gastrolith which consisted primarily of chitin and calcium carbonate hemispheres. The 10 sequential detachment behavior was absent when the soluble proteins were removed from gastrolith substrates and the adhesive energy was reduced by more than two orders of magnitude. The sacrificial bonds that provide the large adhesion energies were inferred to multifunctional gastrolith proteins that were able to bind to both chitin and calcium carbonate.
The results are compared to AFM studies concerning the efficiency of poly(ε-caprolactone) (PCL) as a matrix polymer for cellulose nano-composites [2]. Model cellulose micro-spheres grafted with PCL were prepared via ring-opening polymerization (ROP). Force measurements between the functionalized particles revealed the adhesion to be highly dependent on contact time due to a diffusion controlled mechanism. Moreover, an increase of the temperature to 60 °C (close to T_m for the PCL-graft) greatly enhanced the adhesion at the polymer-polymer interface demonstrating the importance of entanglements in the annealing of composite materials.

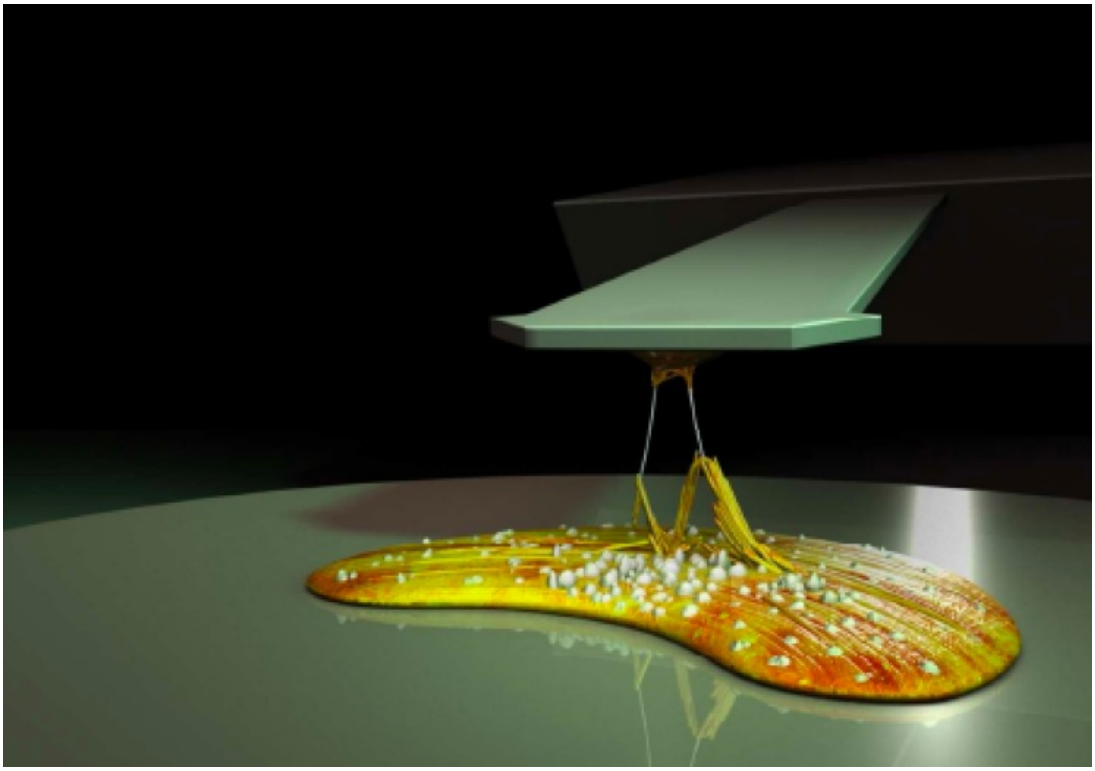

Fig. 1: An artist impression of the experiment. [1]

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TWO-LEVEL HIERARCHICAL SUPERHYDROPHOBICITY WITH MULTIPLE WETTING STATES

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Nature offers great examples on how to make non-wetting surfaces. For example, the well-known lotus leaf exhibits superhydrophobicity and has two levels of roughness [1]. We show that hydrophobic surfaces with two levels of roughness can exhibit multiple metastable wetting states. By experiments and theory we demonstrate that simple post arrays can be designed in a way that the "non-wetting" state is more energetically favourable than the "wetting" state [2]. Such system will spontaneously adopt what we call a *micro-Cassie* state of wetting, which manifests itself in a layer of trapped air between the micron-sized roughness features. Furthermore, locally increasing the pressure of the air layer can cause a transition where the micron-level roughness is wetted, but the nanoscale roughness is still in the Cassie-state (see Fig. 1a). We call this state *nano-Cassie*, because of the scale of the roughness features involved.

Free energy change for the transition can be calculated when we know the contact angle for the nanoscale roughness. Force balance considerations show that the micro-Cassie will switch to the nano-Cassie state if adequate local pressure is introduced. Calculating the axisymmetric meniscus shape shows that air pockets will remain between the bottom and the pillar sidewalls. The shape and size of these air pockets determine whether the nano-Cassie state is unstable. If the air pockets grow too large, they will coalesce and a spontaneous transition to the micro-Cassie state occurs. The transition can also be induced by introducing negative Laplace pressure (*i.e.* suction) on the plastron.

We envision that one of the reasons why the lotus leaves have hierarchical roughness could be because it allows the less-wetting state to be energetically more stable.

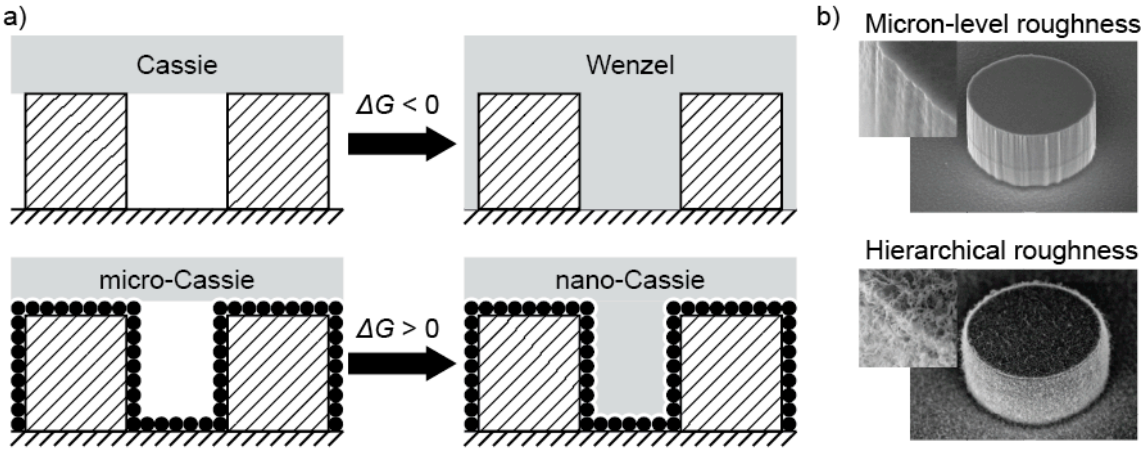

Fig. 1: a) Transition from Cassie state to Wenzel state typically reduces the free energy, but transition from micro-Cassie to nano-Cassie increases the free energy. b) Scanning electron micrographs of surfaces with single-level and hierarchial roughnesses.

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SYNTHESIS AND CHARACTERIZATION OF [ARG-PHE]-OCTAPEPTIDE NANOSTRUCTURES PREPARED *VIA* SOLID-VAPOR PHASE [1]

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Peptides have been used to build nanoscopic self-assemblies endowed of polymorphic diversity and broad range of functionalities.[2,3] These structures bring together interesting properties such as high biocompatibility and selective molecular recognition, which enable their application in fields related to biotechnology. These remarkable characteristics are possible thanks to the organic nature of the building blocks and the incalculable number of peptidic sequences arising from the combination of different amino acids. In this work, we synthesize a novel linear sequence, RF8 (*L*-Arg···*L*-Phe)$_4$, by using the solid-phase peptide synthesis. The synthesis route was the *t*-Boc strategy with Merrifield resin as the polymeric support. Molecular dynamics calculations were carried out to get some insight on the mechanism involved on the stabilization of the sequence. Our findings show that van der Waals interactions and hydrogen bounds are the driving forces on the interplay between the molecular groups. In following, these new building blocks were used to grow ordered nanostructures *via* the *two-step method recently proposed by Park et al*[4,5]. The formation of the structures was examined as a function of the preparation conditions. The parameters evaluated were the nature of the solvent (aniline, water and dichloromethane), the concentration of peptides in the precursory solution and the incubation time. SEM-FEG images reveal the appearance of 1D arrays comprised of fibrilar structures. In addition, it is found a close relationship between morphology and the physico-chemical parameters used in the preparation. The ordering of peptides appears to be strongly dependent on concentration whereas the density of structures per unit area (as well as their orientation) seems to be related to the polarity and dielectric constant of the solvent (Fig. 1). To evaluate the potential of this material for sensing purposes, the strutures were functionalized with polyaniline (PAni) and a electrochemical characterization was carried out.

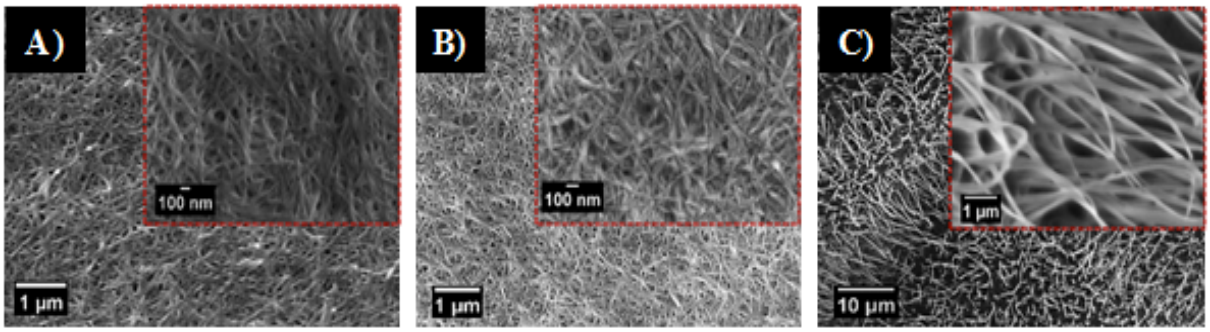

Fig. 1: Nanostructures grown under (A) aniline; (B) dichloromethane and (C) water.

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HIGH-PERFORMANCE ORDERED HIERARCHICAL MESOPOROUS ANATASE TiO_2 VIA BIOMIMETIC SYNTHESIS

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We report a microbial catalytysis (MBC) strategy, by which the ordered hierarchical mesoporous anatase TiO_2 can be synthesized using yeast cells as templates. Biomineralization processes can provide the orderliness and controllability of size, morphology of the mesoporous structure by the biological systems exquisite mediating at ambient atmosphere. The highly regulated and hierarchical mesopores anatase TiO_2 exhibits remarkable electrocatalytic activity and outstanding photocatalytic performances. This hierarchical mesoporous TiO_2 is considered to be promising for applications in biosensor, solar cells, and photoelectrical devices. Additionally, the MBC strategy opens the possibility of creating advanced mesoporous materials the large-scale by a simple and benign environmental route.

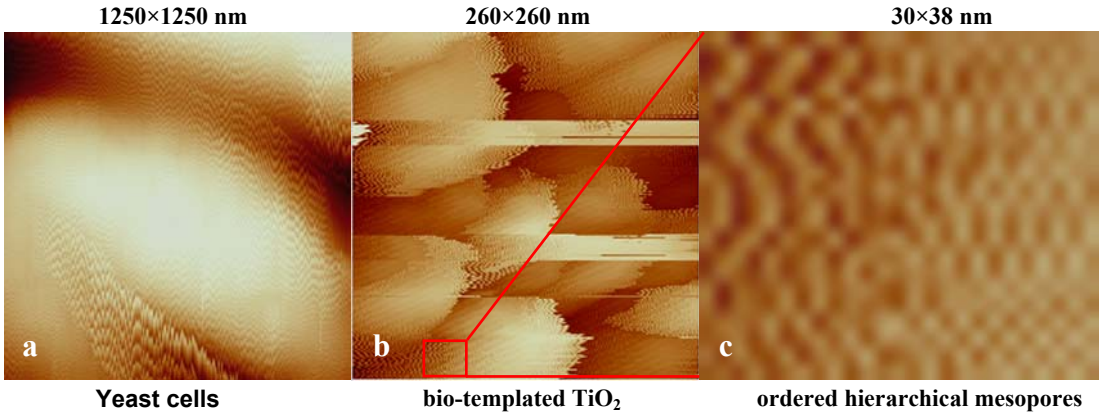

Fig. 1: AFM images of yeast cells (a) and the bio-templated mesoporous TiO_2 (b), the magnified region (c)

MESOPOROUS SILICA AEROGEL -TRICALCIUM PHOSPHATE - HYDROXYAPATITE COMPOSITE CERAMICS FOR ARTIFICIAL BONE SUBSTITUTION

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[3]*University of Debrecen, Department of Solid State Physics, Debrecen, Hungary*

An increasing number of people suffers bone tissue lost each year due to different kind of illnesses or accidents. Missing tissues can be replaced by autografts, allografts, xerografts and grafts of natural or synthetic origin. Artificial materials of controlled strength, chemical composition and pore structure have gained significant attention in the medical practice in the last two decades. Today one of the most rapidly developing areas is the use of resorbable grafts made of tricalcium phosphate, hydroxyapatite, as well as polylactic acid, pmma, collagen or chitosan. The organic materials are most frequently combined with one or more of the before mentioned inorganic active fillers. Most recently the role of silica in living organisms has been revised and now is considered essential for the development of bone tissues. Silica containing calcium phosphate have shown osteoinductivity in human osteoblast cultures in vitro and represents the third generation of bone substituent bioceramics. Pore size distributions in artificial bone substituents are of critical importance. Larger pores and channels in the 100–1000 μm regions are required for bone tissue ingrowth, while smaller pores in the 10–100 μm range conduct the unmineralized fibrous tissue and contribute to material's transport. Our goal was to develop a new kind of osteoinductive artificial graft material based upon a silica aerogel matrix, that can offer the right sizes of pores and mimics the channel structure of the original bone tissues. Sol-gel technology opened the way to the synthesis of mesoporous silica aerogels that can be used as extremely high porosity matrices and, in addition, as excellent drug delivery materials. Most recently we have developed a new technology, which allows us to create silica aerogel composites containing evenly distributed particles of hydroxyapatite and beta-tricalcium-phosphate in combination with disposable porogens from microns to several mm size. Porogens can be used both in random distribution and in highly ordered arrangements.
Aerogels were synthesized with base catalyzed hydrolysis of tetramethoxysilane in the presence of inorganic phosphates and microcrystalline cellulose. Sedimentation of solids was prevented by organic additives. Hydrolysis mixtures were poured into plastic molds; some contained ordered 3D network of disposable cellulose rods or removable stainless steel pins. Alcogels were dried with supercritical carbon dioxide to receive aerogel composites. High temperature heat treatment of the aerogels resulted in inorganic bioceramics of high compressive strength (120 Mpa). These materials still showed the characteristic porosity of aerogels according to SEM examinations. The permeability of the products remained high. In vitro, treatment with simulated body fluid proved the formation of surface hydroxyapatite layer, which is a direct indication of good biocompatibility. Preliminary results of ongoing small animal studies will be presented.

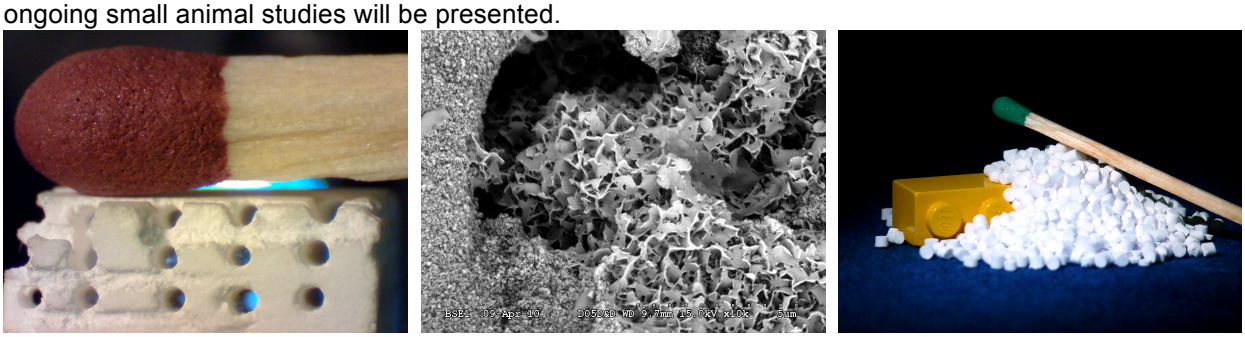

Fig. 1: Pellets (left) and monolithic form (right) of silica aerogel-based artificial bone substitute material. Center SEM picture shows hydroxyapatite crystal formation on the surface after 10-day treatment in simulated body fluid a 37 °C.

Acknowledgments: Financial supports from the following grants are gratefully acknowledged: OTKA 76834 and TÁMOP 4.2.1/B-09/1/KONV-2010-0007

GEOMIMETIC CHRYSOTILE INORGANIC NANOTUBES FOR TECHNOLOGICAL APPLICATIONS

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Hydrotermal synthesis of chrysotile has been utilized primarily for the purpose of obtaining pure chrysotile nanocrystals as a reference standard for ongoing investigation of asbestos citotoxicity and carcinogenicity. A second aim, but not less important, is their use as new synthetic inorganic nanotubes with high potentiality for application in the developing field of nanotechnology [1].
Geomimetic chrysotile inorganic nanotubes is an excellent candidate for constructing nanowires, thanks to its structure. Non toxic chrysotile $Mg_3Si_2O_5(OH)_4$ nanotubes have variable wall thickness dimensions (7,14,21,28,35 nm) corresponding to multiple OT sheets, each 7 nm thick. The central holly canal is 7 nm in diameter. Nanotubes length is variable and controlled, starting from millimetric orders of magnitude [2].
These characteristic features, their crystalline structure without imperfection, highly reproducible and safe for human hearth, [3] make synthetic geomimetic nanotubes excellent candidates to prepare innovative inorganic nanowires, because their holes can host and confine large amounts even of different kinds of nanometric materials. Changing the pH makes possible the electrostatic interaction between different types of filler and the inner surface of the nanotubes, in order to avoid the use of high pressure methods to make nanowires.

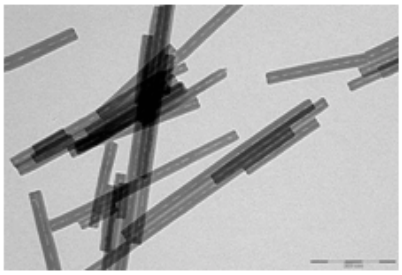

Figure 1

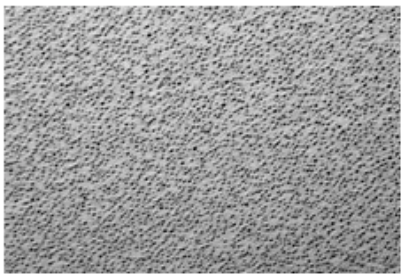

Figure 2

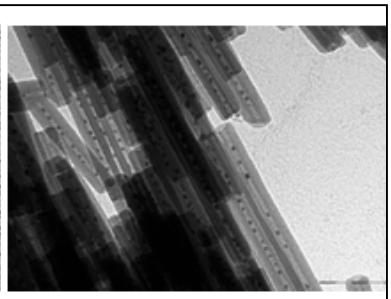

Figure 3

Fig.1: TEM image of synthetic geomimetic inorganic nanotubes
Fig 2 :TEM image of nanoparticles of Ag capped with butyl-mercaptane
Fig.3 :TEM image of synthetic geomimetic inorganic nanotubes filled with Ag nanoparticles

With the aim of preparing the first synthetic geomimetic inorganic nanowires, we have started to synthesize different nanoparticles of metals (Au, Ag, Cu) and metal alloys (Ag/Au, Ag/Cu) surface capped with various thiols, having a constant diameter less than 7 nm and a low tendency to form aggregates. Geomimetic inorganic nanotubes have been filled with previously synthetized metallic nanoparticles obtaining innovative nanowires with outstanding prospects in the field of light-harvesting systems, optoelectronics, photonics and nonlinear optic.

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FABRICATION OF ASYMMETRIC MICROSTRUCTURES AND THE INVESTIGATION OF ITS ANISOTROPIC PROPERTIES

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We demonstrate a facile modified micromolding method to fabricate morphology-controlled elliptical hemisphere arrays (EHAs) by using stretched poly(dimethylsiloxane) nanowell arrays as mold. By intentionally varying the stretching direction, stretching force, size of the colloidal spheres used and other experimental conditions in the fabrication process, we can control the shape, aspect ratio and size of the resulting microstructures. Next, a facile etching method was demonstrated to fabricate silicon elliptical pillar arrays (Si-EPAs) with unique anisotropic optical and wetting characters using polystyrene elliptical hemisphere arrays (EHAs) as mask. Due to the anisotropic morphology of the elliptical pillar, the Si-EPA shows unique anisotropic properties, such as anisotropic surface reflection and anisotropic wetting property. Additionally, through oblique evaporation deposition of Au and selective chemical modification to turn the elliptical pillars into "Janus" elliptical pillars, the "Janus" Si-EPA shows more peculiar anisotropic properties owing to the further increased asymmetry. We believe that these as-prepared elliptical arrays will have potential applications in anisotropic optical and electronic devices.

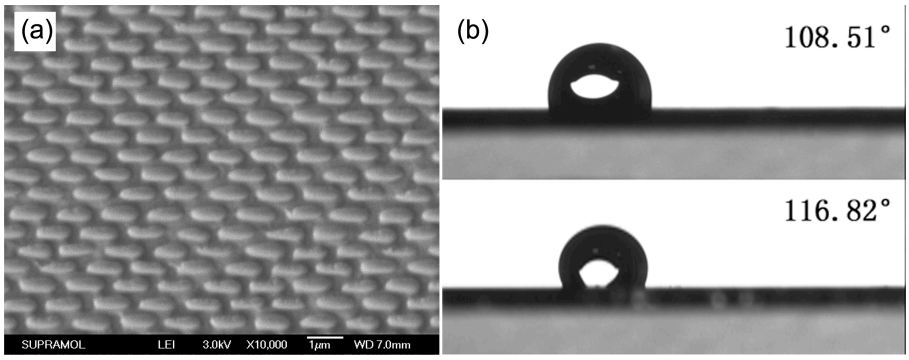

Fig. 1: (a) SEM image of the obtained 2D PS-EHA. (b) Side views of a water drop on the EHA surface taken from two perpendicular directions.

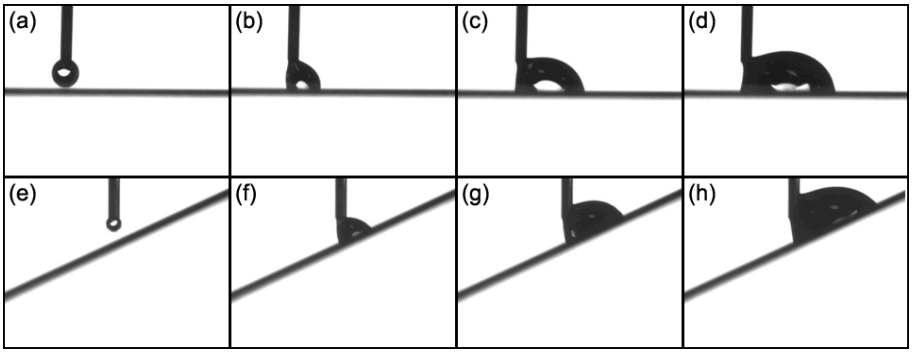

Fig. 2: Photographs of the water drop on the surface of "Janus" Si-EPAs taken at different time (a)-(d) when the substrate was parallel to the horizontal plane and (e)-(h) when the substrate was inclined by about 30° from the horizontal plane. the hydrophilic side was set on the right.

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PHOTONICS WITH DIATOM NANOSTRUCTURED SILICA: AN OVERVIEW

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Several animals, insects, flora and plants are able to manipulate and exploit light in virtue of periodic or quasi-periodic structures at the micro- and nano-scale, mainly (but not exclusively) acting as photonic crystals, which are able to selectively reflect and/or transmit light belonging to specific spectral intervals [1]. Indeed very efficient and elegant photonic nano-structures can be found in nature, such as the complex ultra-structure of exocuticles from beetle *Chrysina gloriosa*, with its ability to selectively reflect left circular polarized light [2].

One of the most versatile photonic architecture present in nature is definitely given by diatom cell walls. Diatoms are unicellular microalgae provided with external, hydrogenated silica investments, the frustules [3]. Frustules are constituted by two valves interconnected by a lateral girdle; the valves and the girdle are characterized by hierarchical, complex and quasi-ordered patterns of pores (the *areolae*) whose dimensions can range from nanometer to micrometer scale (depending on species and on the position in the cell wall structure) [4]. Several studies suggest that these patterns, not only serving a protective function versus mechanical stress, grazing, and external noxious agents, are able to play an active role in manipulation and exploitation of light [5-6], ultimately affecting photosynthetic performance. The impressive similarity of such structures with artificial photonic crystals enforces these hypotheses. The study of optical and photonic properties of diatom frustules is attractive not only for the understanding of the evolutionary advantage represented by pore patterns, but can also lead to applications in, e.g., optical sensing, biosensing and nanotechnology.

In this work we summarize our results obtained in years of study of the optical and photonic properties of centric diatom frustules [7-8], starting from focusing and confinement properties of *Coscinodiscus wailesii* valves to photoluminescent properties of *Coscinodiscus concinnus* and *Thalassiosira rotula* frustules, used as transducing mechanism in chemical and biochemical sensing schemes. Our work has benefited from several optical techniques (optical and confocal fluorescence microscopy, digital holography, steady-state and time-resolved photoluminescence) and different algorithms for the simulation of the propagation of optical fields through the intricate ultrastructure of diatom valves (mainly Wide-Angle Beam Propagation Method and Finite-Difference Time-Domain Method).

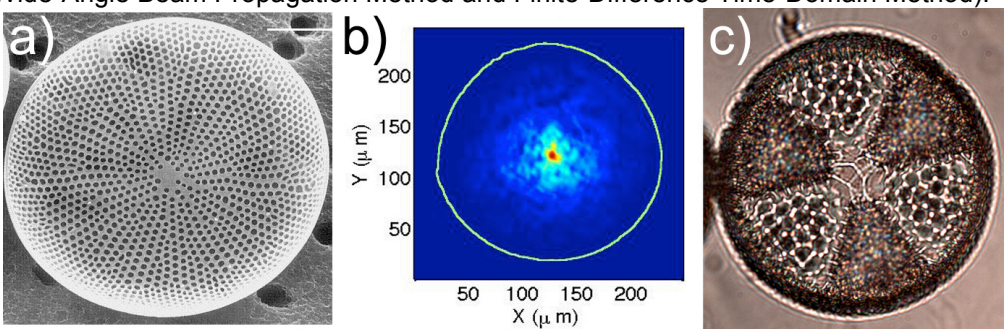

Fig. 2: a): inner view of a C. wailesii valve; b): light confinement from C. wailesii reconstructed by means of digital holography; c: complex spatial distribution of light from Actinoptychus senarius single valve as detected by optical microscopy.

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BIOMINERALIZED CARBONATES AS BINDERS FOR CONSTRUCTION MATERIALS

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Biomineralization is the process in which an organism creates a local micro-environment, with conditions that allow optimal extracellular chemical precipitation of mineral phases. In nature, high strength and durable structures like ant hills and coral reefs are seen to be produced from earth made construction materials through biomineralization. Microorganisms deposit carbonates, one of the most well known minerals and these deposits commonly called microbial carbonate act as binders between loose substrate particles and reduce the pores inside the substrate. Microbial carbonate precipitation has gained interest in the last 20 years in civil engineering because of the selective cementation due to formation of deposits of calcite crystals and these crystals have advantages in special structures and excellent material properties through biomimetic synthesis. Biomineralized calcite binders are formed at ambient conditions with much lower embodied energy as compared to conventional binders. Some of the applications of microbial concrete include improvement in strength of concrete, reduction in permeability and porosity [1], reduction in corrosion of reinforced concrete [2], remediation of cracks in building structures [3] and bio mediated ground improvement [4].

In the present investigation, we have studied the effect of calcifying bacteria *Bacillus megaterium* on durability and strength properties of soil cement blocks. Soil cement blocks were prepared with 8% cement and cured in presence of bacteria. Control blocks received nutrient media without bacteria. The control and treated specimens have been compared at different scales. At macro scale, water absorption, linear expansion and compressive strength have been evaluated. The microscopic studies have been done through SEM – EDX and XRD analysis. Treated blocks showed significant reduction in water absorption, lesser linear expansion and considerable increase in compressive strength due to bacterial calcification and the pores have been reduced within the sand particles. Scanning electron micrography suggested direct involvement of bacteria in calcite crystal precipitation while EDX and XRD analysis proved high amount of calcium in the form of calcite in bacteria treated samples. The present study proved the potential of biominerals as novel way to pave way for eco-friendly, durable, low embodied energy and sustainable construction materials.

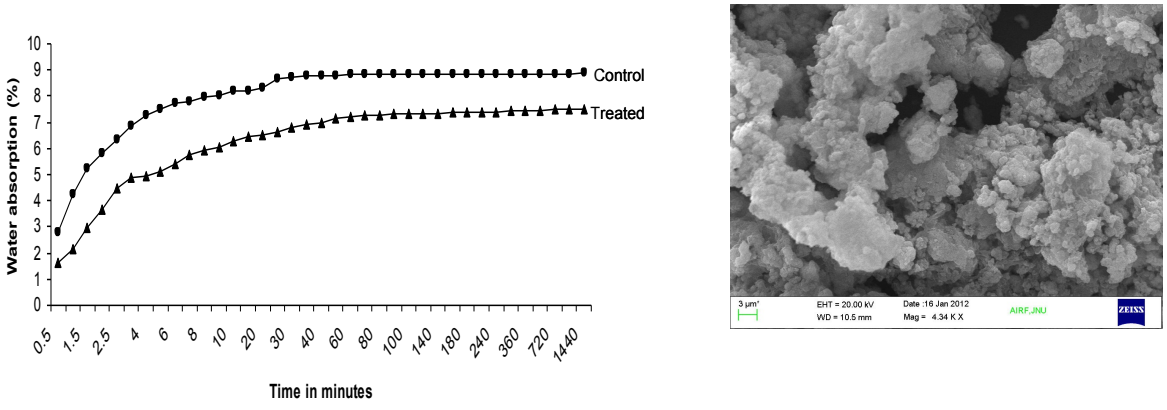

Fig.1: a) Effect of bacterial treatment on water absorption of soil cement blocks b) SEM of calcite crystals formed by B. megaterium in soil cement blocks

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PROPERTIES OF ELECTROSPINNING-PREPARED POLY(ε-CAPROLACTONE)/ L-DIPHENYLALANINE NANOCOMPOSITES

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The electrospinning technique has been widely used to obtain polymer fibers at nanoscopic scale. The poly(ε-caprolactone) - (PCL) - has been extensively studied due to the attractive properties of biodegradability and bicompatibility, as well as flexibility, excellent processability, chemical stability and high mechanical strength.[1] The addition of *L*-diphenylalanine nanotubes in polymer matrices contribute to the formation of nanocomposites endowed of functionalization capabilities. These characteristics open a broad horizon for application in biomedical areas.[2-4] In this work, electrospun fibers containing *L*-diphenylalanine nantubes at concentrations ranging from 2.5% to 15% were investigated. The samples were analyzed by field emission scanning electron microscopy (SEM-FEG), differential scanning calorimetry (DSC), spectroscopy (IR and Raman) and dynamic mechanical analysis (DMA) techniques. SEM images show very regular 1D architectures, with defect-free fibers presenting high homogeneity. Counter-intuitively, we observe that increasing the nanotubes concentration leads to the reduction of the diameter of the fibers. Moreover, DSC results show a diminution on the crystallinity upon addition of nanotubes in the PCL matrix. We have attributed these changes to the formation of new intermolecular bonds, which promote changes in the molecular organization of the polymeric chains. IR spectroscopy confirm the presence of *L*-diphenylalanine nanotubes in the matrix, as observed by the appearance of characteristic peaks at the amine band. Raman spectroscopy also show the grow of the intensities of *L*-diphenylalanine peaks upon peptide concentration. Microscopy images suggest the formation of core-shell structures, where the nanotubes grow within of the PCL fibers, Fig. 1. Studies of the mechanical properties reveal remarkable changes in the elastic properties upon the addition of nanotubes, as shown by a sudden increase on the Young's modulus. In summary, our investigations have demonstrate special properties and high potential of *L*-diphenylalanine-based nanostructures in the formulation of new biocompatible nanocomposites.

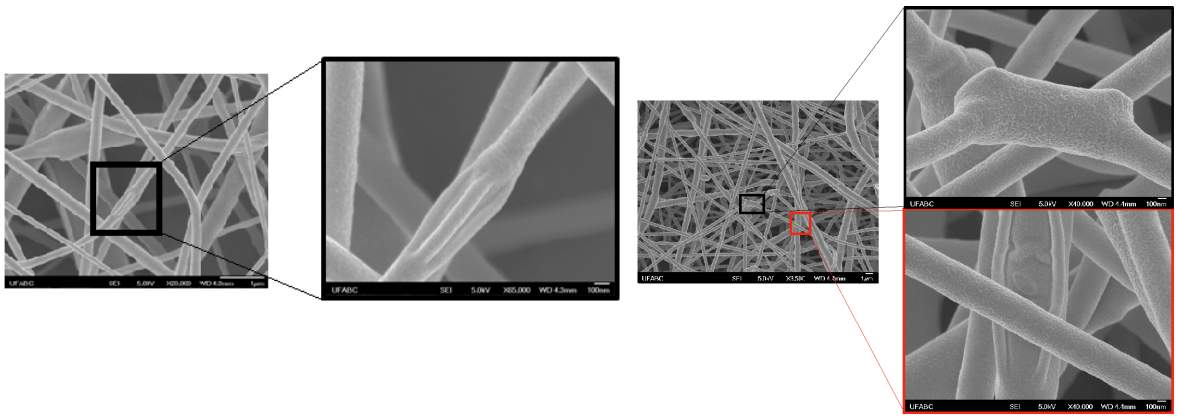

Fig. 1: SEM-FEG images from PCL/*L*-diphenylalanine nanocomposites.

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Acknowledgment: FAPESP, UFABC, INCTBio, CNPq and CAPES

SUPERHYDROPHOBIC/SUPEROLEOPHOBIC SURFACES BASED ON CONDUCTING POLYMERS

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Obtaining super-phobic surfaces for liquid dewetting, water and oil for example, are of both theoretical and practical interest, as has been reported in recent reviews. On the one hand, the wettability of rough solid surfaces is governed by their roughness / morphology at the nano/micro scale and their low surface energy materials presented at the extreme surface. On the other hand, the spreading ability of liquids is governed by their surface tension. Hence, the control of surface morphology, roughness and wettability using liquid probes of various surface tensions is crucial in the development of non-wetting surfaces.
Here, I will present the new advances obtained by our group in the development of superhydrophobic and superoleophobic surfaces by electrodeposition of conductive polymers bearing hydrophobic chains [1-5]. This technique is very versatile to produce non-wetting surfaces. Indeed, the surface morphology and as a consequence the surface wettability can be controlled by not only electrochemical parameters but also by tuning the chemical structure of monomers (Fig. 1 shows an example of exceptional example of surface morphology control, from thin fibrils to extremely long fibers, by replacing oxygen atoms by sulfur ones) [1].

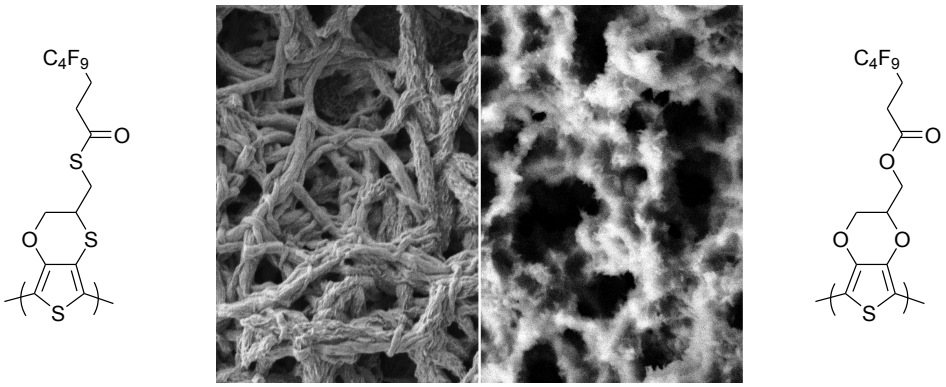

Fig. 1: Surface morphology comparison between two electrodeposited polymers, differing by the substitution of oxygen atoms by sulfur ones, using the same electrochemical conditions.

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Oral Abstracts Session B

BIOINSPIRED ENZYME CASCADES

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The new properties and functionalities that emerge from three-dimensional (3D) structures controlled at the nano-order size are relatively unexplored realms of science. Moreover, biology, chemistry, and materials science may be integrated in order to tailor bioinspired materials. In the present study, it is reported the development and characterization of multi-enzymatic cascades for mimicking living cell glucose metabolic pathways. Glucose oxidase (GOx) and horseradish peroxidase (HRP) were assembled on amine modified polystyrene supports [1]. The first enzyme layer was covalent immobilized to the insoluble support with glutaraldehyde. The second enzyme layer was deposited using the protein conjugation method based on the high affinity "avidin-biotin" interactions. Each enzyme was biotinylated before being added to the nanostructured system and avidin was used as the binder between consecutive enzyme layers. Hence, the alternated bi-enzyme architectures were tested by adding the glucose substrate in buffered water solution and the bio-response was measured by the optical absorbance at 650 nm due to the oxidation of the chromophore (TMB) [2,3]. The results have clearly indicated the bioactivity response of the bi-enzyme 3D-nanostructures and also the dependence to the concentration of the glucose substrate, indicating that it could be considered as a nanosensor. Furthermore, this bi-enzyme concept can be extended to multi-enzyme layer-by-layer systems where the product of each preceding reaction catalyzes and is consumed in the next reaction. In that sense, the novel nanostructured behaved analogously to the energy metabolism of cells resembling an enzymatic cascade which is usually triggered by an initial stimulus or some signalling molecule.

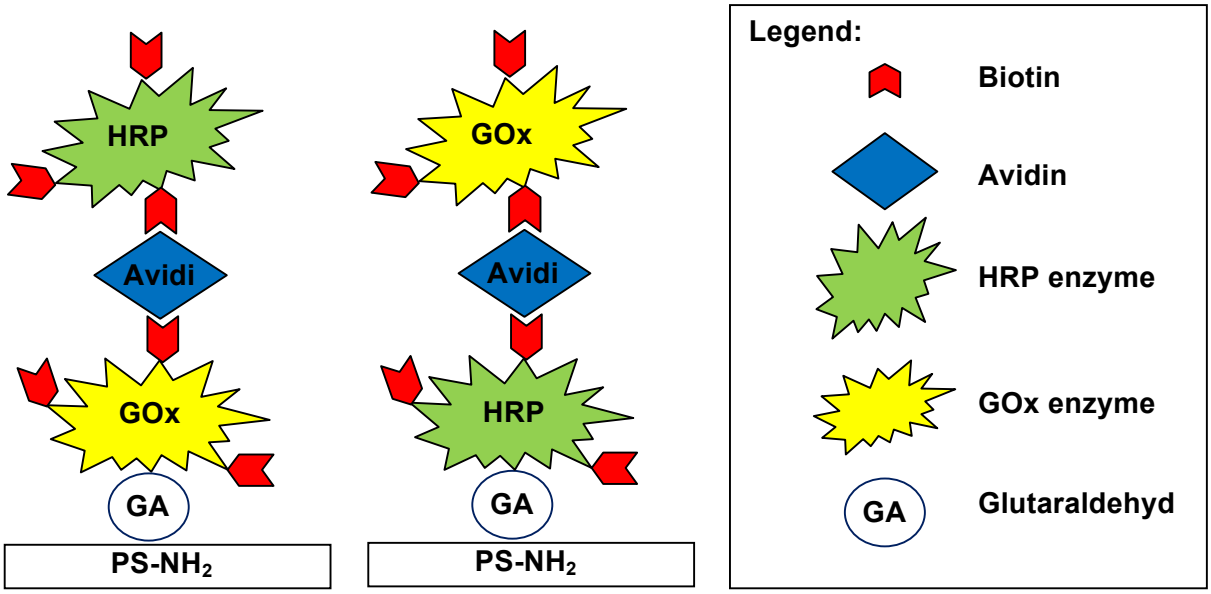

Fig. 1: Schematic diagram of the alternated bi-enzyme architectures.

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FURAN MODIFIED METHACRYLATE HYDROGELS THROUGH DIELS-ALDER CYCLOADDITION IN AQUEOUS MEDIA

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Due to the future depletion of fossil resources, the design of new macromolecular structures capable of substituting the currently employed petroleum-derived monomers is receiving an increasing interest. In this way, furfural is a first generation furan compound prepared from polysaccharides bearing penthoses which allows obtaining a wide range of monomer structures whose only specificity is that they all bear the furan ring [1].

The pronounced dienic character of the furan ring makes it suitable for Diels-Alder reaction, a thermoreversible cycloaddition between a diene and a dienophile which offers the opportunity to recover the starting reagents by heating [2]. These kinds of materials are promising in terms of recycling and self-healing capacity of the polymers. Moreover, the reaction conditions are mild, usually no additives or catalysers are required and it runs in absence of side reactions [3]. Therefore, the Diels-Alder reaction has been widely studied in organic synthesis and represents a suitable candidate for the development of "green" synthetic strategies [4].

This work was focused on the design of new chemically-crosslinked hydrogels through the Diels-Alder reaction in aqueous media. The starting polymer chosen was poly (2-aminoethyl methacrylate) which was modified both by reaction with furfural to obtain the suitable diene and recurring to protective chemistry using a DA adduct (exo-3, 6-epoxy-1, 2, 3, 6-tetrahydropthalic anhydride) to prepare protected maleimides. Bisfunctional dienophiles were also synthesized through the modification of water soluble Jeffamines with maleic anhydride.

The aim of this work was to obtain a new crosslinked network following two different strategies. On one hand, starting from two complementary water soluble polymer precursors, and, on the other, by crosslinking the furanic polymer with bisdienophiles (figure 1). The synthetic pathways for the introduction of the diene and the dienophile into the structures were established and the products obtained characterized. The Diels-Alder reaction was carried out successfully in water under mild conditions without the addition of catalysers and confirmed by FTIR spectroscopy. This whole synthetic approach allowed for the preparation of hydrogels in aqueous media, based in part on renewable resources and with thermoreversible properties.

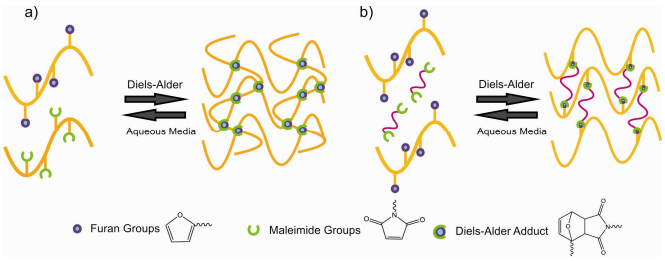

Fig. 1: Hydrogel formation by Diels-Alder reaction from a) polymeric precursors and b) bisdienophiles

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This contribution is dedicated in memoriam to Professor Iñaki Mondragon who collaborated on this work and passed away recently.

BIO-INSPIRED ADHESIVE MATERIALS FOR CELL-BASED CANCER DIAGNOSTICS

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Circulating tumor cells (CTCs) have become an emerging “biomarker” for monitoring cancer metastasis and prognosis. Although there are existing technologies available for isolating/counting CTCs, the most common of which using immunomagnetic beads, they are limited by their low capture efficiencies and low specificities. By introducing a three-dimensional (3D) nanostructured substrate – specifically, a silicon-nanowire (SiNW) array coated with anti-EpCAM – we can capture CTCs with much higher efficiency and specificity. The conventional methods of isolating CTCs depend on biomolecular recognitions, such as antigen-antibody interaction. Unlikely, we here proposed that nanoscaled local topographic interactions besides biomolecular recognitions inspired by natural immuno-recognizing system. This cooperative effect of physical and chemical issues between CTCs and substrate leads to increased binding of CTCs, which significantly enhance capture efficiency. Recently, we have also developed a 3D cell capture/release system triggered by aptamer enzyme, which is effective and of “free damage" to capture and release cancer cells. The bio-inspired interfaces of cell capture and release open up a light to rare-cell based diagnostics, such as CTCs, fetal cells, stem cell and so on.

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TUNABLE, DYNAMIC AND ELECTRICALLY STIMULATED LECTIN-CARBOHYDRATE RECOGNITION ON A GLYCAN-GRAFTED CONJUGATED POLYMER

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Multivalent and oligomeric carbohydrates found in cell surface glycoproteins and glycolipids play an important role in numerous normal and pathological biological events. Lectins are multimeric glycan-binding proteins. The glycan-lectin recognition regulates such biological processes as cell proliferation, adhesion, immune responses, cell-cell interaction and communication, among others. Various glycan arrays and glyconanostructures utilizing fluorescence, surface plasmon resonance, quartz crystal microbalance, among others, have been developed to measure the lectin-glycan binding affinity, analyze recognition mechanism and perform pathogen sensing. Electrically active platforms based on conjugated polymers have been utilized to understand and evaluate biomolecular recognition events, including complementary DNA binding and aptamer/protein recognition due to the great current interest for the development of low cost, portable lab-on-a-chip bioanalytical and diagnostic devices. The connection between glycan and pathological event allows this pair a promising target. In addition, there has been a growing interest to study the electrical stimuli on physiological characteristics of cells, such as neurons, for potential application in tissue engineering. Integration of the glycan-mediated cellular information with electrical stimulation would be important to decode the cellular-cellular interaction within such supplications.

Herein we describe the specific, tunable, dynamic and electrically stimulated recognition of a biomolecule (Concanavalin A) and a conducting polymer, poly(3,4-ethylenedioxythiophene) (PEDOT), whose surface is modified by the complementary ligand, α-mannoside as shown in Fig. 1. PEDOT is a widely used organic electronics material and it also demonstrates a great potential for biological applications because of its superior biocompatibility and long-term stability in aqueous solutions. By using electropolymerization technique, we successfully demonstrate a tunable and dynamic recognition platform which provide an electrically stimulation feature.

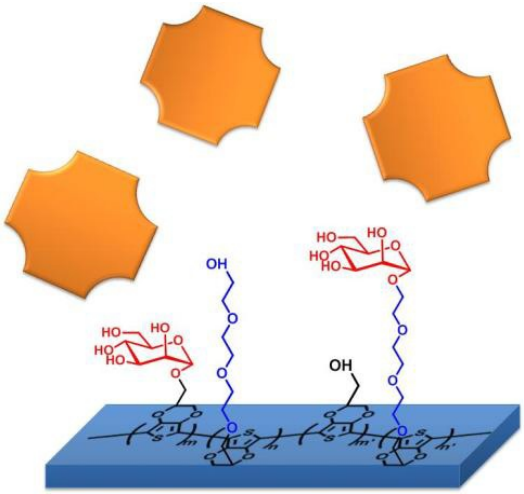

Fig. 1: Mannose-functionalized PEDOT biointerfaces

ELECTROCHEMICAL APPROACH FOR SUPEROLEOPHOBIC SURFACES

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The obtaining of surfaces with superoleophobic properties is a very recent field of investigation. Oils have a low surface tension and thus a high ability to wet any surfaces. Surfaces that can repel oils must have peculiar surface roughness, as double scale (micro and nano) surface structuration and are consequently very difficult to produce.
The elaboration of superoleophobic surfaces usually involves multi-step processes to create the surface morphology and to modify the extreme surface with fluorinated materials. Our research group is able to produce superhydrophobic and superoleophobic surfaces using a controllable, easy to implement, fast and one-step method: the electrochemical deposition of conducting polymers. [1]
In this study we could control the micro and nanostructuration by varying two parameters: 1) the molecular structure of the monomer and 2) the electrodeposition method (imposed potential or current) to obtain a wide range of properties including exceptional anti-oil properties: a contact angle of 150° with hexadecane. [2]
We present here results obtained from a pyrrole-based platform molecule (the general procedure is presented in figure 1). The electrodeposited polymer films were characterized by static and dynamic contact angle measurement with various probe liquids, optical profilometry and scanning electron microscopy.

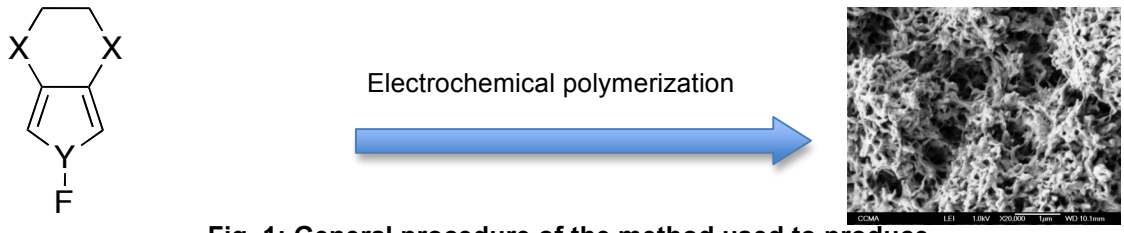

Fig. 1: General procedure of the method used to produce superoleophobic surfaces

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OXIDATION OF GLUCOSE COMBINED WITH ENZYMATIC DIOXYGEN REDUCTION IN BIOFUEL CELLS FOR SUSTAINABLE ENERGY PRODUCTION

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The development of stable devices able to convert chemicals to electrical energy from bio-sourced fuels, to supply both implantable devices and microelectronic apparatus, is of great interest since it could be at the origin of new insights concerning the treatment of illness [1] and convenient solution to provide energy for microelectromechanical systems [2]. These devices use enzymes as biocatalysts and are called "enzymatic biofuel cells" (Fig. 1). However, the current performance of these devices is still low to be applicable and is limited by low enzyme loading, low enzyme stability and by weak electron transfer between the enzymes and the electrode.

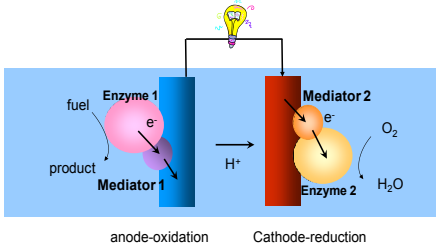

Fig. 1: Enzymatic biofuel cell (BFC) principle.

We are currently working on the development of ecological biofuel cell which uses the renewable resource glucose as fuel. The chemical transformation of glucose, by the enzyme glucose oxidase, is coupled with the enzymatic reduction of O_2 to water to produce electrical energy.
This work focuses on improving the design and performances of the Biofuel Cells. The main interests of this system are the selectivity of the enzymes, and the operation of the device in mild conditions. The efficiency of the biofuel cell is supported by various techniques of enzyme immobilization (grafting, adsorption, entrapment in polymer matrix) and means for optimizing their electrical connection to the conductive support [3, 4].
Besides, to improve the electrical performances, we have synthesized novel carbon nanofibers by electrospinning (Fig. 2) to increase the amount of immobilized enzymes and to facilitate electron transfer between the enzymes and the electrode, which is related to the intrinsic transport property of the carbon fibers [5]. The electrochemical activity of the biofuel cell is evaluated by electrochemical experiments (such as linear polarization curve, chronoamperometry). The results present the influence of the two critical issues, output and cell stability, in the development of BFCs.

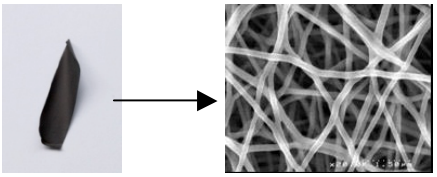

Fig. 2: Image of the carbon nanofibrous mat (d = 90 µm) and SEM characterization.

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BIOINSPIRED ENCAPSULATION OF LIVING *CHLORELLA* CELLS WITHIN PROTECTIVE AND FUNCTIONALIZABLE SILICA/TITANIA ARTIFICIAL SHELLS

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The artificial shells of hard inorganic materials on individual living cells would protect the encapsulated cells against physical deformation and chemical hazards, and control cell division. These emerging properties could be combined with cell-surface functionalizations for applications to cell-based sensors and assays as well as for fundamental studies on cellular metabolism in the single-cell basis. In this work, individual *Chlorella* cells were encapsulated within a SiO_2-TiO_2 nanocomposite shell in a bioinspired fashion that utilized a designed peptide, $(RKK)_4D_8$, as a catalytic template for formation of both SiO_2 and TiO_2 on the cell surface. The cell viability was maintained by the procedures, and the division of the encapsulated *Chlorella* cells was controlled by the SiO_2-TiO_2 shell. The SiO_2-TiO_2 shell in our system effectively dissipated heat energy and maintained the cell viability about 4.5-fold better than the unencapsulated one. For the cell manipulation and immobilization, magnetic nanoparticles were successfully embedded in the shell. In addition, the incorporation of TiO_2 to the shell made it possible to anchor the ligands of interest to the shell in a cytocompatible fashion. Therefore, the combination of biological SiO_2 and abiolgical TiO_2 for the shell formation gave more tunability of the artificial shells compared with the SiO_2 or TiO_2 shells only.

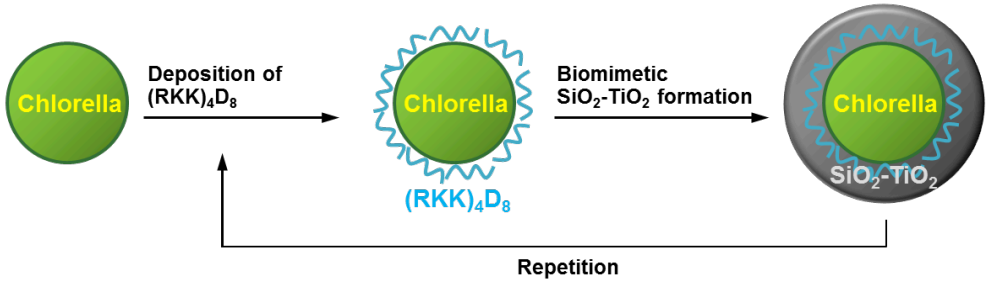

Fig. 1: Schematic diagram for individual encapsulation of *Chlorella* cells within silica/titania nanocomposite shells.

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A ROLE FOR POLYMER BRUSHES IN BIOSENSORS

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Polymer brushes have many desirable characteristics such as the ability to tether molecules to a substrate, or change the properties of a surface. In the past few years they have garnered much attention for their involvement in microelectronics, nanofluidic devices, biosensing, and other areas of nanotechnology [1-4]. We are investigating several types of biosensors that can be enhanced through the incorporation of polymer brushes. Two examples are given here.

The first biosensor (figure 1) entails an electrochemical detection system based on the antibody catalyzed water oxidation pathway (ACWOP) which takes advantage of the intrinsic ability of the primary antibody to generate hydrogen peroxide when in the presence of singlet oxygen and water [5]. Using a simple solution assay and electrochemical detection, we can measure the H_2O_2 produced and thus all antibodies bound to the device. As a means of amplifying the signal, polymer brushes have been integrated to bind the antibodies to the surface as well as to prevent non-specific adsorption of other antibodies or contaminants that may be present in the test fluid. Because of the ability to tailor the polymer brushes to specific antibodies, a broad range of viruses can be investigated. Additionally, we have established certain patterning methods that allow us to incorporate both the polymer brushes and a photosensitizer (required for production of singlet oxygen) onto the same surface. This multifunctionalized surface provides both signal amplification and background reduction.

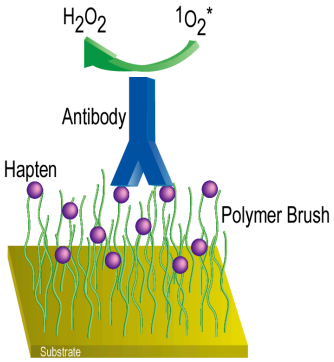

Fig. 1: Schematic depiction of immunosensor polymer brush platform based on the ACWOP.

A second example includes a PEDOT:PSS based microelectrode which measures neuron activity for the study of brain function. This device requires the tethering of certain biomolecules for specific charge exchange reactions to occur between the biological media and the conducting polymer sensor. Our goal is to use polymer brushes as a way of anchoring these molecules to the electrode surface. We have begun to explore different methods of binding an atom transfer radical polymerization (ATRP) initiator to the PEDOT:PSS surface and growing polymer brushes without damaging or significantly reducing the conductivity of the native film.

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THE DESIGN OF 3D LIVER MODELS USING BIOPOLYMER BASED POLYELECTROLYTE MULTILAYERS

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A critical challenge in hepatic tissue engineering is the design of polymeric scaffolds that can maintain liver cell phenotype. Our focus is to design biopolymer based scaffolds to assemble three-dimensional liver models. Such scaffolds must not only enhance cellular adhesion but must also elicit liver-specific functions over an extended period of time [1]. Towards this goal, we have designed novel detachable polyelectrolyte multilayers (PEMS) using biopolymers such as chitosan and hyaluronic acid. We report the design of detachable, free-standing, and transparent PEMs assembled with chitosan and hyaluronic acid (HA). The detachable nanoscale self-assembled PEM recreates the Space of Disse, an interfacial region found in liver by matching the thickness (400–600 nm). Robust free-standing PEMs were obtained at 12.5 and 15 bilayers. The corresponding thickness for dry 12.5 and 15 bilayer PEMs was 400 ± 29.7 nm (n = 6) and 654 ± 17.5 nm (n = 6), respectively. Both 12.5 and 15 bilayer free-standing HA/chitosan PEMs were robust, and could be manipulated for further experimentation.
AFM was used in force-distance mode to measure the mechanical properties, specifically the Young's modulus, of dry and hydrated 12.5 and 15 bilayer PEMs. For each sample, three different force-distance curves were obtained at different locations.
The curves obtained from AFM were fit to a Hertz model modified for a conical indentation and the Young's modulus was estimated. Hydrated measurements were obtained with PEMs immersed in phosphate buffered saline solution. The Young's modulus of crosslinked 12.5 and 15BL PEMs decreased to 41.79 ± 3.65 kPa and 38.15 ± 2.62 kPa, respectively, upon hydration. The mechanical properties of the hydrated PEM matched modulus values reported for bulk liver tissues *in vivo*. The optical transmission of crosslinked 12.5 and 15 bilayer hydrated PEM ranged between 99.1 and 99.9% transmission, indicating these PEMs are virtually transparent under hydrated conditions. The surface topography of a substrate that is intended for culturing cells can have a significant impact on cellular function, proliferation, and phenotype. Therefore, the surface topography of the 12.5 and 15 bilayer PEMs was investigated using an atomic force microscope in contact mode and the substrates were found to be smooth.
Using the detachable PEM, a 3D liver mimic that incorporates three of the major hepatic cell types; primary rat hepatocytes, liver sinusoidal endothelial and Kupffer cells (liver macrophages) has been assembled. The 3D multi-cellular culture maintains the phenotypes of all three cell types simultaneously. The PEM layer facilitates exchange of signaling molecules between the different cell types. We have successfully assembled liver-mimetic cellular cultures using detachable PEMs.

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BACTERIA-TEMPLATED SYNTHESIS OF HOLLOW NANOSTRUCTURES

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Hierarchical hollow nanostructures have attracted a great deal of attention because of their conspicuous physicochemical properties that differ markedly from those of bulk materials and potential for wide-ranging applications especially in optical, electronic, magnetic, and sensing devices ranging from photonic crystals to drug-delivery carriers and nanoreactors. These materials are often prepared by the template synthesis method. Bacteria have evolved a large variety of well-defined stunning morphologies controlled at the micro- or even nanoscopic level, among which cocci, bacillus, vibrios, spirillum, and square bacteria acting as templates can lead to the formation of corresponding three-dimensional hollow nanostructures, some of which are currently unattainable through any other chemical method, and materials of such structures may have striking properties.

We have reported two bacteria-templated routes for the synthesis of hollow nanostructures by hydrothermal [1] and sonochemical [2] methods respectively. Here, using bacteria as morph-biotemplates, we report two approaches for the controlled syntheses of metal chalcogenide porous hollow nanostructures by a sonochemical method [3] and of hollow TiO_2 micro/nanostructures based on surface sol-gel process [4]. Biomorphic PbS and ZnS hollow nanostructures have been successfully synthesized with two species of bacteria cocci and bacillus as morph-templates. A preliminary study on the light-harvesting properties of PbS and ZnS hollow spheres revealed that the hollow and porous structure is clearly far more favorable for the absorption of light than solid counterparts. Furthermore, photocatalytic studies of ZnS nanostructures by degradation of acid fuchsine under solar irradiation have proved that the hollow structures possess superior photocatalytic activity to the corresponding solid counterparts. The various hollow TiO_2 micro/nanostructures have been synthesized with bacteria as templates based on surface sol-gel process to further study the structural effect on photocatalytic hydrogen evolution properties. The hollow TiO_2 structures exhibit superior photocatalytic hydrogen evolution activities in the presence of sacrificial reagents under UV and visible light irradiation. The hydrogen evolution rates on average is 3.6 times higher than that of the corresponding solid counterpart and 1.5 times higher than P25-TiO_2. These versatile approaches provide effective routes for the further extensive study of the distinct properties imparted by hollow nanostructures and extends their application potentials in photocatalysis and solar energy storage/conversion.

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DESIGN OF FUNCTIONAL BIO-BASED POLYESTERS

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Poly(3-hydroxyalkanoate)s (PHAs) represent a class of natural aliphatic polyesters accumulated by many bacteria as intracellular energy and carbon storage materials when they are subjected to stress conditions. They constitute an enlarged family of bacterial polyesters that can be considered as promising biopolymers for biomedical and environnemental applications, due to their biodegradability and biocompatibility. Using various substrates, a wide variety of PHAs can be synthesized, differing notably by the length of their side chains. The length of side chains strongly affects the physical properties of PHAs.
In this contribution, the versatility of PHAs in the design of a wide variety of biodegradable and/or biocompatible macromolecular architectures will be illustrated. First, unsaturated PHAs were chemically modified *via* the transformation of pendant double bonds into epoxy, carboxyl, hydroxyl or alkyne groups. Moreover, these reactive functions could further be used for grafting hydrolyzable polylactide (PLA) or poly(ε-caprolactone) (PCL) as well as hydrophilic poly(ethylene glycol) through two distinct mechanisms, namely either a "grafting from" method or a "grafting onto" approach (direct esterification or "click" chemistry). PHA-*b*-PEG and or PHA-*b*-poly(2-methyl-2-oxazoline) block copolymers were also synthesized by "click" chemistry, while totally degradable block copolyesters were generated by ring-opening polymerization of D,L-lactide or ε-caprolactone. Our study has also demonstrated an efficient green UV-photografting method for covalently modifying the surface of PHBHV film with HEMA and MAA in aqueous media and in heterogeneous conditions.

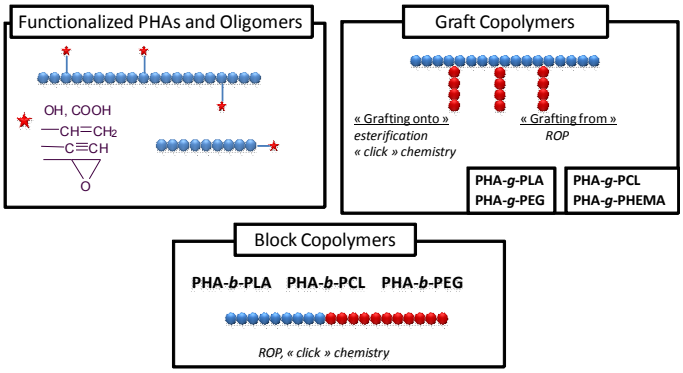

Fig. 2: PHAs-based polymersomes

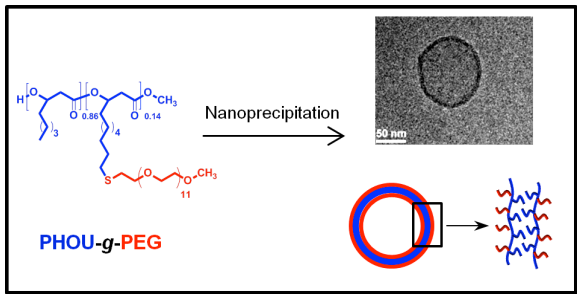

Fig.1: Well-defined macromolecular architectures based on PHAs

The potential of functional PHAs and relative copolymers in the drug release area, tissue engineering and anti-adhesive activity has been illustrated through the investigation of cell adhesion on functionalized PHA films, doxorubicin release from stable nanoparticles, anti-bacterial properties, micelles and polymersomes formations. These studies have shown the potentialities of introducing functional groups or segments either on side positions or on a terminal position of PHAs to fine-tune their physico-chemical properties, so as to reach specific applications. The PHA-based frameworks can be adapted to other biomedical applications through tailor-making topology, composition and functionality of macromolecular architectures to fit prerequisites corresponding to a specific device.

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IRON-BASED BIOMIMETIC HYBRID MATERIALS FOR CATALYTIC APPLICATIONS

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The development of low-molecular weight iron-based catalysts aiming to mimic key-structural and-functional properties of natural iron-enzymes is a topic of considerable interest [1-3]. In heterogeneous catalysis, solid-supported catalysts have attracted much research attention since a) they have increased stability and selectivity and b) they can be easily recovered from reaction media and reused, minimizing effluent contamination [3,4]. Inorganic supports are generally preffered *vs.* organic supports, because they are more robust. Among the support used to immobilize bioinspired catalysts, inorganic support such as SiO_2 are prefered due to their low cost, availabiltiy, mechanical robustness and chemical inertness.
Immobilization of the catalyst through covalent bond is generally preferred vs. immolilization through electrostatic interaction of [charged catalysts] with [charged support] for several reasons. [i] Adsorbed catalysts often suffer from leaching of the active complex to solution. Zero-leaching is guaranteed *vis* covalent grafting. [ii] Immobilization prevents agglomeration of the catalyst. [iii] Immobilization can potentially lead to substrate shape-selectivity because of specific interactions of the substrates with the inorganic matrix [3].
This technology can be exploited to develop **hybrid-biomimetic catalytic materials [HBCM]** [5-10]. Here, we present a coherent mechanistic approach on the development of new HBCMs bearing two families of [i] **Fe-heme** or [ii] **Fe-non-heme** oxidation catalysts immobilised covalently on SiO_2 particles. We ll present catalytic and spectroscopic data which show that [i] the non-heme **Fe-HBCMs** are efficient on alkene oxidation with H_2O_2, much more stable than the corresponding homogeneous catalysts and recyclable. Electron Paramagnetic Resonance [EPR] data allow monitoring of the catalytic evolution of the Fe-centers. [ii] We present also a heterogenised catalyst developed by covalent immobilisation of the iron-porphyrin complex FeR_4P on SiO_2. The heterogeneous FeR_4P-SiO_2 catalyst is very efficient for oxidative decomposition of pentachlorophenol (PCP) and highly recyclable in the presence of imidazole. EPR data provide direct evidence that high-valent iron species $[R_4P^{+\cdot}Fe^{IV}=O]$ are formed in the heterogenised FeR_4P-SiO_2 system. Complete dechlorination of the initial PCP is achieved. [iii] Decomposition of formic acid towards hydrogen generation over immobilized Fe-base catalyts will be also presented.

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A BIOLOGICALLY INSPIRED COPPER/TOPAQUINONE-LIKE DUAL CATALYTIC SYSTEM FOR THE CHEMOSELECTIVE AEROBIC OXIDATION OF AMINES TO IMINES

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Imines are versatile synthetic intermediates in a variety of organic transformations and are essential pharmacophores in numerous biologically active compounds [1]. Although great progress has been made in the past decade for the synthesis of imines, the development of new efficient environmentally benign procedures continues to be a challenging and active area of research. In particular, simulation of the functions of amine oxidase enzymes that govern the metabolism of amines may lead to the development of biomimetic catalytic oxidation of amines to imines under mild conditions. In this respect, we recently found that an electrogenerated *o*-iminoquinone species $\mathbf{1_{ox}}$ (see Fig. 1) was able to replicate the activity and specificity of copper-containing amine oxidases (CuAOs) toward primary amines [2-4]. The catalytic cycle produced *N*-alkylidenealkylamine as the product of amine oxidation through the ionic pyridoxal-like transamination process reported for CuAOs. This $\mathbf{1_{ox}}$-mediated electrocatalytic oxidation of primary amines allowed the generation of unstable imines, under metal-free conditions, without any stoichiometric reagents, at ambient atmosphere. These conditions are particularly favorable for using the imine in situ for further reactions. For example, we have recently developed a facile one-pot metal-free $\mathbf{1_{ox}}$-mediated oxidation-imine formation-reduction sequence for the atom-economical chemoselective *N*-alkylation of benzylic primary amines with amines, allowing the synthesis of benzylic secondary amines under mild conditions [5].
Nevertheless, it seemed doubtful that our electrochemical procedure will ever be able to compete with more conventional chemical approaches at a large preparative scale. In contrast, the process would be most attractive if $\mathbf{1_{ox}}$ could be generated through aerobic oxidation of $\mathbf{1_{red}}$. So, inspired by the enzymatic reaction of CuAOs, and by recent breakthroughs on the aerobic oxidation of amines to imines, we have demonstrated that a synergistic combination of copper and topaquinone-like catalyst $\mathbf{1_{ox}}$ constitutes a novel approach to imines from primary amines, under very mild conditions, which include dioxygen in air as the oxidant, together with ambient temperature and pressure [6]. The oxidation process starts with atmospheric oxygen as reported in Fig. 1, and continues in a cascade-like manner, by passing the oxidation potential of oxygen through copper salt to the organic *o*-iminoquinone mediator $\mathbf{1_{ox}}$, which finally oxidizes the amine substrate. This atom-economical process tolerates the presence of various reactive functional groups and allows selective cross-coupling of two amines.

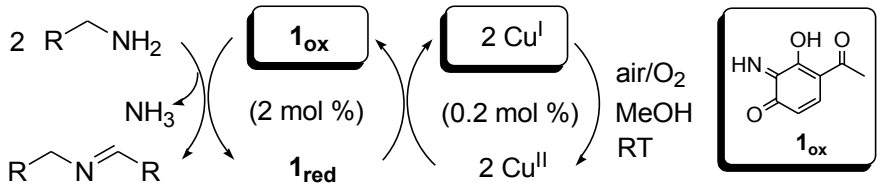

Fig. 1: aerobic oxidation of primary amines to imines catalyzed bu Cu^{I}/*o*-iminoquinone $\mathbf{1_{ox}}$

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STUDY OF HYBRID FILM CONTAINING PEPTIDE NANOSTRUCTURES AND COPPER COMPLEX(II) FOR ELECTROANALYTICALS DETERMINATIONS

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Self-assembled peptide nanostructures are electronically insulating as are most biomaterials derived from natural amino acids. To obtain additional properties and increase the applicability of peptide nanomaterials, some chemical modifications can be performed and materials can be functionalized to form hybrid compounds. We described the formation of *L*-diphenylalanine nanotubes (PNTs) with cyclic-tetrameric copper(II) species containing the ligand (4-imidazolyl)-ethylene-2-amino-1-ethylpyridine $[Cu_4(apyhist)_4]^{4+}$ in the Nafion membrane on a glass carbon electrode (GV) surface. This copper(II) complex has been studied as structural and functional models for the active centers of copper(II) containing redox enzymes. The electrochemical properties of the PNT-$[Cu_4(apyhist)_4]^{4+}$/Nafion film were characterized using cyclic voltammetry and square-wave voltammetry for hydrogen peroxide reduction and dopamine oxidation and showed high electrocatalytic activity toward the two substances. For dopamine oxidation (Figure 1A) under the optimum conditions, the square-wave voltammetry peak height was linearly related to the DA concentration over two concentration intervals, viz., 5.0-40 μmol L^{-1} and 40-1000 μmol L^{-1}. The detection limit was 2.80 μmol L^{-1} (S/N = 3), and ascorbic acid did not interfere with the DA detection [1]. After that, we have studied the influence of the equilibrium in the electrocatalytic activity towards of H_2O_2 reduction in the development of an amperometric sensor. This strategy proved successful, and the electrochemical behaviour of the all complexes formed within the Nafion coatings was characterized. We also provide evidence that its related cyclic tetranuclear imidazolate-bridged complex [2] acts as a catalysts for the intramolecular (Figure 1B), two-electron of H_2O_2 reduction. These results suggested that this hybrid bioinorganic system provides an attractive advantage for a new type of electrochemical sensors. The detection sensitivity was found to be enhanced by use of PNTs.

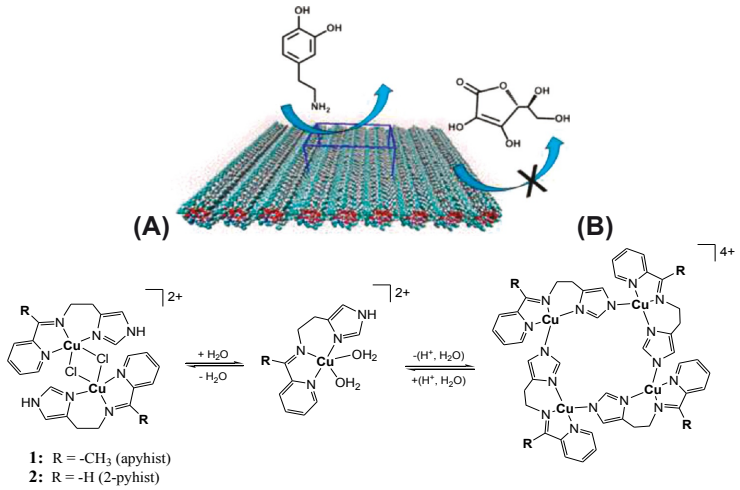

Fig. 1: (A) Scheme dopamine oxidation. (B) Representation of equilibrium in solution.

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SYNTHESIS OF HYDROPHOBIC STARCH USING CATALYTIC APPROACH

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In the actual context of shortage of petroleum resources, biomass is considered as a renewable alternative for fuels and chemical substitution. At IRCELYON, we focus on the development of catalytic transformations of biomass into materials, chemicals or fuel.

Due to its large availability and low cost, native starch has been used for long time in the preparation of different products. However, the use of native starch in many industrial applications suffers of several drawbacks such as easy thermal decomposition, high retrogradation or low shear stress resistance. To circumvent these limitations, native starch can be chemically, physically or enzymatically modified. Such modified starches exhibit specific properties depending on the type of modification. In particular, hydrophobic starch can be obtained through protection of the free hydroxyl groups of glucoside units with ester or ether moieties.

We developed a catalytic route based on the telomerization of diene with native starch [1]. This palladium-catalyzed reaction allowed to the formation of octadienyl chain as the main product *via* dimerization of two molecules of 1,3-diene with hydroxyl groups of the starch. 1,3-butadiene, the simplest diene, is a convenient diene as it is easily available at low price. Isolated [(π-allyl)Pd(TPPTS)$_2$]Cl catalyst was shown to be efficient in the telomerization of methanol in the presence of water as well as for the telomerization of starch in a water/iPrOH mixture under very mild conditions [2]. Moreover, the telomerization of butadiene with starch can also be performed in pure water if surfactants are present in the reaction media [3].

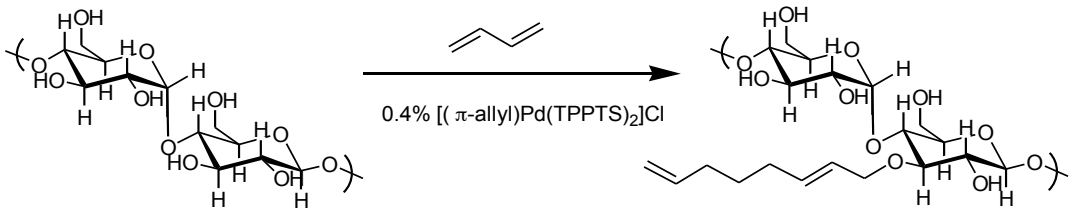

Fig.1: Telomerisation of starch with butadiene

After optimization of the reaction conditions, we prepared substituted starch keeping the texture of the granular native starch (20-100 μm). Physico-chemical analysis (contact angle measurement, rheological properties, water adsorption-desorption isotherms) showed that even at low degree of substitution (DS < 0.1), the properties of the modified starch were strongly affected and hydrophobic materials which can be useful for specific applications were prepared.

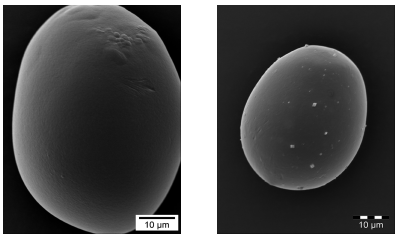

Fig. 2: SEM picture of starch before and after reaction

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MICROBIAL PLASTIC FACTORY: NEW LACTATE-BASED AND RELATED BIOPOLYMERS

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Microbial Plastic Factory (MPF) has been established for direct production of the bio-based polymers with desired properties from renewable carbon sources. Currently, the engineered lactate (LA)-polymerizing enzyme (LPE) allowed us to develop the one-pot synthetic system for LA-based polymers [1, 2]. As shown in Fig. 1, the MPF carrying LPE can be involved in the carbon-recyclable system organizing synthesis and degradation of the value-added polymers [3]. We have been focusing our interest on creating attractive new extremely high enantio-pure biopolymers with varied LA fractions in MPF. Fine regulation of LA fraction in the two- and three-component copolymers has been successfully achieved in metabolically engineered *Escherichia coli* by combination of enzyme evolutionary engineering and metabolic engineering [4-6]. *Corynebacterium glutamicum* also served as a useful MPF to produce PLA-like polyester from glucose [7]. I will present the concepts to perform pathway modifications for enhanced LA generation and further evolution of LPE. Especially, thermal and mechanical properties of the newly synthesized "biological" copolymers with various LA fractions will be discussed with regard to comparison with those of counter parts, "chemical" PLA and "biological" P(3-hydroxybutyrate) [8, 9]. Most recently, advanced MPF for production of the new polymers incorporating new 2-hydroxy acid monomers, glycolate [10] and 2-hydroxybutyrate [11] will be also introduced. This suggests very broad capacity of LPE polymerizing a variety of 2-hydroxy acid monomers.

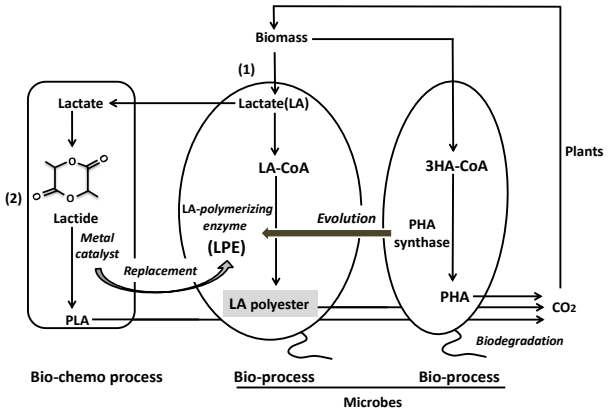

Fig. 1: Microbial Plastic Factory for Biopolymer Production [3]

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SYNTHESIS OF BIOBASED BUILDING BLOCKS FROM VEGETABLE OILS: TOWARD PLATFORM CHEMICALS

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Polyurethanes (PU) are versatile plastics which occupy an important position in the world market of high performance synthetic polymers, with a global consumption around 14 million tons in 2000. Polyurethanes are traditionally prepared by reacting an oligomeric polyol and a diisocyanate. Whereas the isocyanate component is always derived from petrochemical feedstocks, the polyol component could come from biobased resources. The use of biobased polyols for the manufacture of polyurethanes is a real positive point for the envi-ronmental impact of polymers. It is all the more interesting to use biobased polyols in PU synthesis since polyols represent the major part of PU, generally between 60 to 70% in weight of PU.

Vegetable oil-based polyols could be synthesized from varied oils which, except castor oil, have to be chemically fonctionnalized to meet the polyurethane production requirements. Transesterification and epoxydation are already industrially used for the production of polyols from oleochemicals. The thiol-ene reaction represents another interesting toolbox for the functionalization of unsaturated vegetable oils. Indeed, this reaction of "click chemistry" allows photochemical or thermal initiation, undemanding synthesis conditions thanks to the insensitivity to oxygen inhibition, and leads to high yields with basic purification procedures. Firstly, our team used reactive molecules bearing hydroxyl or amine functions to synthesize tailored modified vegetable oils. Secondly, we extended the use of thiol-ene on vegetable oils to the synthesis of new polyamine and polyacids building blocks for polymer synthesis. From polyfunctional building blocks made from vegetable oil, we followed two pathways to synthesize biobased polyurethanes: firstly, we used polyols in standard polyurethane synthesis to produce partially bio-based polyurethanes. Then, we synthesized biobased dicyclocarbonate and biobased oligomeric polyamines, that react together to form isocyanate-free polyurethanes. It is all the more interesting since cyclocarbonates could be synthesized by functionalization of glycerol, produced in large quantities by the transesterification of natural triglycerides as part of bio-diesel production. This method leads to totally biobased polyurethanes. In both cases, polyurethane materials synthesized were characterized by physicochemical analyses and thermal characterizations.

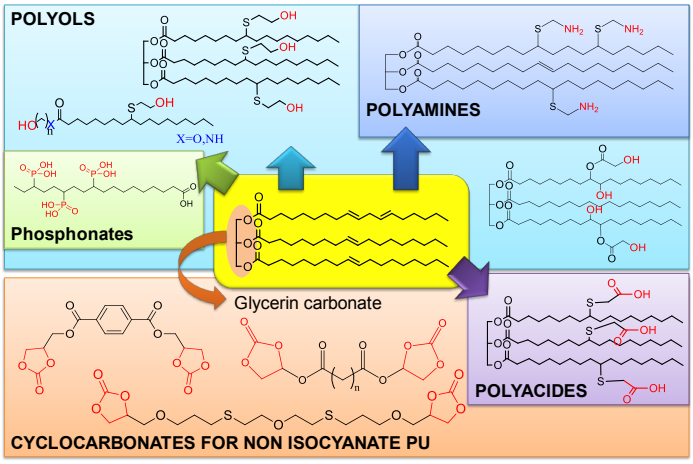

Fig. 1: various vegetable oil-based building blocks

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BIO-INSPIRED CATIONIC POLYMERIZATION OF ISOPRENE AND ANALOGUES

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In 2010, 10.4 million tons of Natural Rubber (NR, polyisoprene-PI- 100% 1,4-*cis* of high molar mass, $>10^6$ g/mol) were produced in the world, which represents more than 45% of total elastomers worldwide consumption. NR is a strategic material as its excellent properties are not mimicked by synthetic rubbers.

Whereas isoprene is the monomer employed for the chemical synthesis of PIs, isopentenyl pyrophosphate is the monomer used for the biosynthesis of NR (IPP, Figure 1). After its transformation into dimethylallyl pyrophosphate (DMAPP) via an isomerase, few molecules of IPP are added to DMAPP via a *trans*-prenyl transferase. Finally, IPP is polymerized by a *cis*-prenyl transferase to yield NR. From the polymer chemist point of view, these enzymatic processes can be seen as electrophilic additions, comparable to those operating in cationic polymerizations. Both during initiation and propagation reactions, the pyrophosphate moiety is released to give an allylic carbocation able to add IPP yielding a tertiary carbocation (Figure 1). One α proton is then eliminated with the pyrophosphate moiety giving back an allylic pyrophosphate chain terminus. The only difference between *trans*- and *cis*-prenyl transferase is the type of double bond generated during the process. It has been shown that divalent cations are necessary to trigger the reaction. Considering a "cationic-like" pathway, they could act as Lewis acids, assisting the cationation (1, 2).

The goal of our work is to investigate new synthetic routes, which are inspired by the biosynthetic pathway in order to find new alternatives for the production of new NR-like synthetic rubbers. To this end, the cationic polymerization of isopentenol (3) or isoprene (4-6) has been studied in the presence of different allylic initiators and Lewis Acids, this latter playing the role of the divalent cation in the biosynthetic route. For example, it was shown that allylic alcohols associated to $B(C_6F_5)_3$ were able to initiate the cationic polymerization of isoprene. This latter was investigated varying the conditions (solvent, T°C, concentration, additives). It will thus be presented and discussed our last results concerning the synthesis of polyisoprenes and analogues by cationic polymerization.

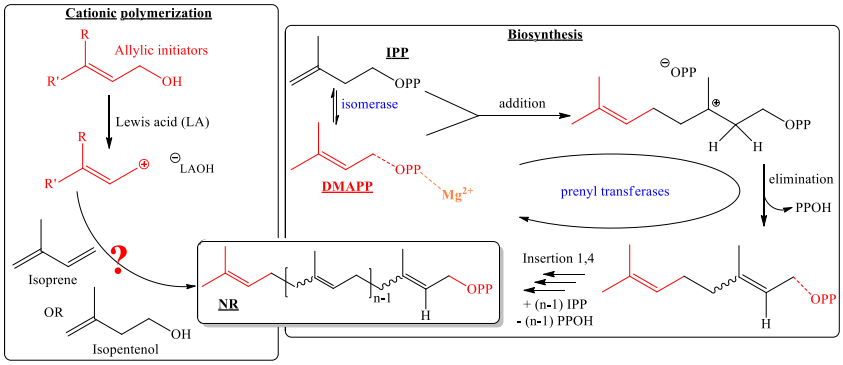

Fig. 1: Biosynthesis and bio-inspired synthesis of NR

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GREEN CHEMISTRY: BIO-BASED RENEWABLE MATERIALS

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The Green Chemistry Centre of Excellence promotes the application of green and sustainable technologies, particularly those that can be used to deliver products that meet consumer and legislation requirements. Generation of novel materials from bio-based renewable resources is an important area of research in the Centre. Utilising naturally abundant bio-resources and in particular agricultural and food by-products, we have developed a range of materials which take full advantage of the chemical composition, rich functionality and structure in plant metabolites and other biomass. Three examples of bio-based materials and their inherent chemistry will be discussed:

1. **"Starbons"** - Polysaccharides have high inherent functionality, difficult to introduce in petroleum plastics. This presents a great opportunity for new materials, but access to this functionality is hindered by the low surface area of the raw materials. Simple physical and chemical modifications enabled development of a range of novel porous materials with applications in catalysis, adsorption, chromatography, and composites, where these materials offer superior performance characteristics. These include an exciting new class of mesoporous materials "Starbons " which have surface properties ranging from starch-like to carbon-like [1].
2. **"Switchable Adhesives"** - A multi-partner industrial project on development of green switchable adhesives for carpet tiles. In the UK alone 53,000 t p.a. of carpet tiles are manufactured. With current adhesives used in the product, components are not separable and therefore not recyclable. Over 90% of post-consumer tiles and waste from manufacture end up in landfill sites. Modified starch switchable adhesives developed in this project enable separation and recycling of components providing a green alternative to currently used synthetic polymers. The new adhesives have excellent mechanical performance and additionally are flame resistant removing the need for auxiliary flame retardant chemicals [2].
3. **"Bioboards"** – A multi-partner collaborative industrial project focused on the development of green structural panels, wholly based on agricultural by-products. The project applies biorefinery concepts to generate materials, energy and chemical products from renewable recourses. It aims to develop generic methodologies applicable to a variety of raw materials, reducing feedstock dependence, impact on biodiversity and providing added value to farmers. Structural panels used in furniture and construction industries are made of wood bound with synthetic organic resin. Availability of FSC certified wood is limited and the binders, typically formaldehyde/isocynate-based, are toxic/harmful in production and/or use. In this project the following bio-based intermediates are used:
   (a) Aggregate: Lignocellulosic plant residues avoid the need for FSC virgin wood
   (b) Binder: New bio-derived inorganic silicates, generated from waste biomass combustion ashes, are a chemical product with many applications [3]; they provide non-toxic, non-volatile, chemically and biologically resistant and inherently fire-retardant binder.
   (c) Hardener: Suitable chemical functionalities can be naturally present/derived in situ in the aggregate or sourced from by-products of bio-fuels production.

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DIRECT CONVERSION OF NATIVE LIGNIN TO FUNCTIONALITY CONTROLLABLE POLYMERS

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Lignin is the most abundant and complicated natural polymer on the earth, forming long-term carbon flow in the ecosystem. Lignin is very important aromatic source for creating the next generation without petroleum. In order to create sustainable human society without disturbing the ecosystem, sequential transformation system of lignin must be established, leading to cascade-type utilization from composites- to monomer levels.

Lignin is a hybrid type polymer composed of glycerol units (aliphatic) and polyhydric phenol units (aromatic). A key for sequential functionality control is how to control C1- (7%) and C2- (50%) aryl ethers selectively. The cleavage of C1 aryl ethers results in the transformation of polymer structures from network to linear, and that at C2 leads to depolymerization to dimer level. A sequential transformation system developed in Funaoka Lab includes three steps: 1st step; the selective control of C1 structures, leading to 1,1-bis(aryl)propane type units, 2nd step; the selective control of C2 structures using intramolecular switching devices [1,1-bis(aryl)propane-2-O-aryl ether units], leading to the change of molecular weight and phenolic activity, 3rd step; phenolic activity control by demethylation of methoxyl group to give polyhydric phenol units.

The polymers, lignophenols, derived from native lignin through C1 control are multi-functional lignin based materials. Sequential applications designed originally are shown below: Recyclable composites with cellulose, biopolyesters, and inorganic materials (glasses, metals), Raw materials for recyclable polymers, Detachable adhesives, Switching devices for material recycling, Electromagnetic shielding materials, Carbon molecular sieving membranes, Enzyme supports for bioreactors and affinity chromatography, Adsorbents for proteins and metals, Performance control agents for lead-acid battery and enzymes, Photoresists, Antioxidants, UV barriers, Solar cell sensitized with lignophenols.

The system plants designed specially for the sequential transformation have been constructed in Japan: 1st and 2nd systems; batch systems, 3rd and 4th systems; continuous and compact systems.

A frontier industrial network initiated from lignocellulosics is proposed for the post-petroleum generation.

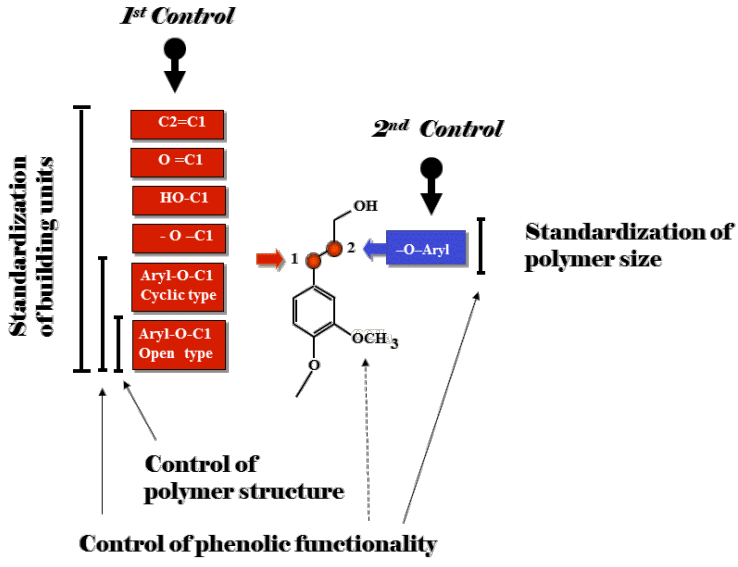

Fig. 1: Sequential transformation of lignin.

Fig. 2: 4th System plant for converting lignocellulosics to lignin-based polymers and soluble sugars.

CHITOSAN –OLIVE OIL FILMS MODIFIED WITH CELLULOSE NANOCRYSTALS

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Public concern about environmental pollution have stimulate the interest in developing products from renewable resources, economically competitive and with minor environmental impact [1]. In particular, chitosan, the de-N-acetylated form of chitin, is a natural cationic polysaccharide, non-toxic, biodegradable and available commercially, that has been employed in a variety of applications [2]. It is a well-known biopolymer that acts as stabilizer of hydrocolloids - lipids mixtures, promoting emulsion formation and interfacial stabilization.
On the other hand, CNC (cellulose nanocrystals) have attracted significant attention because they are renewable and environmentally benign, naturally abundant, biodegradable, biocompatible and have excellent mechanical properties.
The objective of this work is to improve the resistance to water of chitosan films by the addition of hydrophobic compounds such as olive oil and at the same time, to improve the mechanical response by the incorporation of cellulose nanofibers.
Film preparation: Chitosan (CH) solution (2 %wt/vol in acetic acid 1% vol), glycerol (Glycerol/CH=0.28), CNC (1.79 % wt water suspension) were mixed and dispersed with the aid of a homogenizer (Ultra-Turrax) and a sonifier (BRANSON sonifier 250). After that, the lipid fraction was incorporated as olive oil (OO)/CH weight ratio of 0.1. The stable emulsions achieved by using both, homogenizer and sonifier were poured into Teflon Petri dishes and dried at 35 ºC for approximately 10 h in a convection oven.

Table 1. Tensile properties and total soluble matter of CH and CH-OO films reinforced with CNC.

% CNC	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	TSM (%)
CH				
0	134.6 ± 16.6	8.4 ± 0.6	19.6 ± 3.4	14.25 ± 3.88
3	406.6 ± 98.3	12.6 ± 1.1	9.2 ± 2.7	13.58 ± 2.91
5	328.3 ± 89.1	10.7 ± 1.5	7.9 ± 3.3	10.81 ± 0.60
7	346.7 ± 89.3	12.6 ± 1.5	7.9 ± 0.8	10.95 ± 0.30
12	351.7 ± 164.6	8.9 ± 1.6	5.1 ± 0.9	7.21 ± 2.06
CH-OO				
0	189.3 ± 49.0	8.9 ± 2.3	13.8 ± 6.3	11.34 ± 0.25
1	220.7 ± 43.1	8.9 ± 1.8	9.8 ± 3.5	7.66 ± 1.08
2	360.6 ± 29.2	8.7 ± 1.8	5.9 ± 2.8	7.59 ± 1.33
3	239.7 ± 84.1	10.5 ± 2.2	11.2 ± 2.1	5.461 ± 2.41

From the total soluble matter (TSM), it is clear that both, nanocellulose and olive oil addition lead to reduced final values, due to complex interactions generated between constituents. In fact, the presence of oil not only leads to strong associations with chitosan but also entraps part of the plasticizer, avoiding its loss in aqueous medium, as was reported in a previous publication [3]. Moreover, the presence of CNC in the emulsion films enhances this behavior, indicating a synergistic effect between both additives.
CNC performs as reinforcing filler for both, plasticized chitosan films with and without olive oil. However, these trends are valid up to CNC contents of about 3 % wt, at higher concentrations the effect of the lipid addition (enlarged tensile strength and elongation at break [3]) prevails over the reinforcement one, probably because some filler agglomeration begins to take place. In fact, the dispersion of the crystals in the film forming emulsion became more difficult as the CNC content increases and homogeneous films containing both, olive oil and higher cellulose concentrations could not be obtained.

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FLUOROUS-MODIFIED NATURAL SURFACTANTS AS COMPATIBILIZERS FOR FLUORINATED PHASES AND MATERIALS

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Hydrophobins (HPBs) [1] are a family of small (ab. 10 kDa), exceptionally surface active proteins, bearing a hydrophilic/hydrophobic structure which effectively makes them natural Janus particles. Because of their high surface activity and film-forming capabilities (see Fig. 1, left), they have been used as foaming and coating agents, adhesion promoters and emulsifiers of fatty oils. More recently, they have been shown to exfoliate and disperse graphene sheets in aqueous environment without need for chemical modification of graphite, ultimately leading to bionanocomposite materials [2].
Nevertheless, HPBs have not yet been significantly exploited at the interface between water and fluorous oils. We first report here a study on the behaviour of HPBs in these systems and as stabilizers for fluorous-oil-in-water emulsions [3], showing their potential for biomedical applications, microfluidics and emulsion fluoropolymerization.

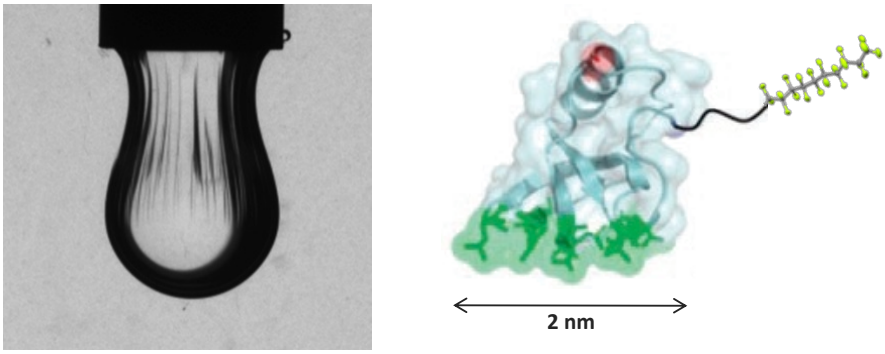

Fig. 1: (left) HFBI film formation at the interface between water and perfluoropolyether; (right) Schematic representation of the fluorinated hydrophobin F-HFBI.

Expanding on this research, we prepared a hydrophobin derivative which was chemically modified by the covalent attachment of a fluorophilic segment [4]. This new engineered protein (F-HFBI, see Fig. 1, right) combines the film forming capabilities of hydrophobins with the superior surface activity of fluorous surfactants. We show here the remarkable surfactant properties of this unique polyphilic protein and its assembly behaviour at liquid-liquid and solid-liquid interfaces. In particular we focus on the enhanced affinity of F-HFBI towards hydrophobic solid surfaces (both lipophilic and fluorophilic), which appears to involve a combination of common hydrophobic interactions and fluorous-fluorous partition effects.

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NEW BIOMIMETIC SURFACE TREATMENT BASED ON SAPONIFIED VEGETAL OIL

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Conversion surface treatments of metals play a major role in protecting them against corrosive aggressions during their temporary exposure to atmospheric conditions (storage, transport). Nevertheless, these kinds of process have non-negligible environmental impacts, related to the use of toxic chemical reagents and the induced solid/liquid wastes. Thus, the increase of the environmental regulations (REACH legislation) leads to research on more environmentally-friendly and more efficient surface treatment processes. In this framework, the use of linear saturated carboxylic acids with long carbon chain, extracted from vegetal oils (colza, sunflower, ricin, etc.) is an interesting alternative to much corrosion inhibiting formulations, because of their low cost and their easy and secure use. They are known to form protective layer made of crystallized insoluble metallic carboxylates.
In this work, whole ricin oil is saponified by using a “soft” process (without organic solvent, T<40 °C) to obtain directly liquid formulations that can be easy diluted in aqueous solutions.
From a morphological point of view, metallic surfaces (iron, zinc) immersed in these saponified ricin oil containing formulations exhibit a bioinspired shape. Whereas metallic carboxylates plates are classically observed on surface of carboxylated metals (like after phosphatation process), the metallic surfaces treated in our diluted formulations show nanotubular morphology, comparable to self-assembled structures (epicuticle) observed at the extreme surface of some plants (Fig.1)

a) b)

Fig. 1: Comparison of surface morphologies observed at extreme surface of hydrophobic leafs (Eucalyptus Gunni) (a) and at zinc surface treated in diluted saponified ricin oil (b).

This biomimetism can be extended to the functional point of view. These tubular nanostructures induce noteworthy hydrophobobic properties that have been evaluated by contact angle measurements. Actually, the air is trapped in the nanoporosities of the surface film which increases the barrier effect against water (“lotus” effect). Therefore, the corrosion resistance of such a nanotubular organo-metallic framework, investigated in a corrosive medium simulating atmospheric condition by classical stationary electrochemical methods as well as electrochemical impedance spectroscopy, is greatly improved and comparable to usually used surface treatments.

LIPASE-CATALYTIC PRODUCTION OF ESTOLIDES IN NON-AQUEOUS MEDIA FROM *TRANS*-HYDROXY-FATTY ACIDS

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Hydroxy-fatty acids production has been a tedious task for years. It is well known that bacterial lipoxygenases from some strains of Pseudomonads could produce hydropxyperoxy-fatty acids as intermediates of hydroxy-fatty acids. When *Pseudomonas aeruginosa* 42A2 is cultivated in a mineral medium using oleic acid as carbon source, two different hydroxy-fatty acids are produced with a yield of 43% conversion of the substrate [1,2]. 10(*S*)-hydroxy-8(E)-octadecenoic acid ((10*S*)-HOME) is synthesized with a volumetric productivity of 0.237 $g \cdot l^{-1} \cdot h^{-1}$ and 7,10(*S*,*S*)-dihydroxy-8(E)-octadecenoic ((7*S*,10*S*)-DiHOME) with a value of 0.267 $g \cdot l^{-1} \cdot h^{-1}$. Subsequently, (10*S*)-HOME and (7*S*,10*S*)-DiHOME are extracted from the supernatant and purified to a 91 and 96% of purity, respectively.
Estolides, polyesters from fatty acids, have been synthesized for years in a chemical synthesis. Over the last years, lipases have emerged as a powerful tool in organic synthesis and diminish the rough conditions in which estolides were produced [3]. Novozyme 435, lipase B from *Candida antarctica*, is used in this work due to its capability to interact with different kind of substrates and reaction media. For the first time, an apolar reaction media, *n*-hexane, is used to synthesize *in-vitro* estolides from *trans*-hydroxy-fatty acids derived from oleic acid with a reaction yield of 30%.
With the aim to determine the structure of the olygomers formed, liquid chromatography-mass spectrometry and MALDI-TOF-mass spectrometry with a lithium DHB matrix [4], a non-conventional structural technique, have been adapted to obtain simpler mass spectra. Ricinoleic acid estolides were used to check the validity of these two structural determination techniques. According to that, estolides composed of two units of (10*S*)-HOME were synthesized. Finally, a screening of various lipases and another apolar organic solvent, *iso*-octane, was assayed to find out better reaction yields.

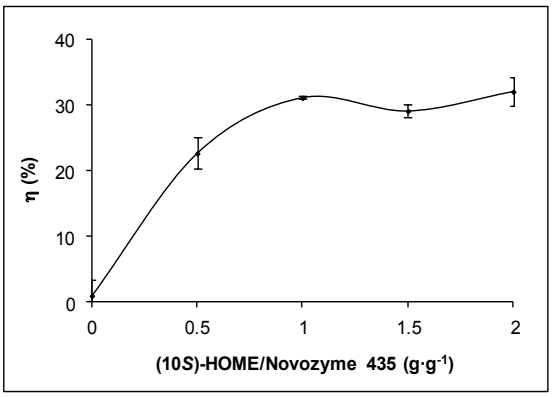

Fig. 1: Optimized conditions in the estolides production.

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COHERENT SYNCHRONIZED REACTIONS OF SUBSTRATES OXIDATION BY HYDROGEN PEROXIDE

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There are many types of interaction between reactions. Conjugated processes are the most demonstrative of reciprocal influence and interaction of two or more reactions.
The event when one reaction speeds up the proceeding of another reaction is shown up in non-chemical induction: e.g. via initiation or synthesis of a catalyst in a reaction for another reaction. The mutual influence of reactions synchronously proceeding in a system includes a much broader range of events than chemical induction suggests.
This work shows practically all kinds of possible reaction interactions, which part may be united in a general idea of interference of chemical reactions. The notion of interference includes mutual intensification or weakening of the reactions: for instance, the rate of primary reaction product formation decreases, whereas the rate of secondary, conjugated reaction product formation increases. Currently, the mutual influence of reactions synchronized in time and space will be taken for interfering chemical processes.
With this approach conjugated processes appear to be a particular case of interfering processes [1]. As guided by the idea on chemical interference, one may define many kinds of interactions between reactions. Finally [2], the phenomenon may be formulated as follows: the event consisting of the fact that reactions synchronously proceeding in the chemical system are mutually intensified or weakened is called chemical interference, i.e. interaction (e.g. interfering) reactions must be coherent.
In the present work various types of possible interactions are discussed. Some of them are united by the general idea of chemical reaction interference. The ideas on conjugated reactions are broadened and the determinant formula is deduced; the coherence condition for chemical interference is formulated and associated phase shifts are determined. It is shown how interaction between reactions may be qualitatively and quantitatively assessed and kinetic analysis of complex reactions with under-researched mechanisms may be performed with simultaneous consideration of the stationary concentration method. Using particular examples, interference of hydrogen peroxide dissociation and oxidation of substrates is considered.

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WATER-BORNE POLYURETHANE DISPERSIONS BASED ON RENEWABLE RESOURCES

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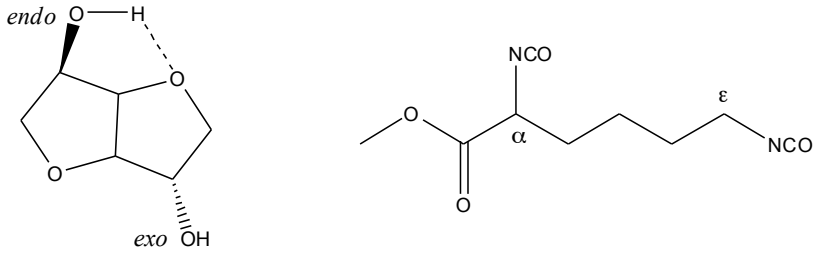
Water-borne polyurethane dispersions (PUD) are environmentally benign products for coating applications [1-3]. To prepare PUDs, first a low molecular weight isocyanate-terminated PU prepolymer is synthesized by reacting polyols with diisocyanates either in the melt or in solution. In addition to the main PU building blocks, an internal stabilizing agent is built into the prepolymer chains to facilitate the formation of water-borne dispersions through a solvent assisted process. High molecular weight PUD products are realized by reacting the isocyanate-terminated prepolymers with diamine chain extenders. Since the organic solvent is distilled off from the dispersions, the VOC (volatile organic compound) content is minimized.
Biomass-based PUDs are being developed in recent years [4-6]. For example, soybean oil, sun flower oil or castor oil-derived diols have been developed for polyurethane synthesis. However, these renewable diol-based polyurethanes still contain non-renewable diisocyanates and diamines. The availability of dimer fatty acid-based diisocyanates, diols and diamines, lysine-derived diisocyanates and triisocyanates as well as other bio-based diols such as 2,3-butane diol, makes it possible to prepare water-borne PUDs predominantly based on renewable resources.
In our research, we focus on a) studying the reactivity of two asymmetric biomass-based PU building blocks, namely isosorbide and methyl ester L-lysine diisocyanate (MELDI) (Fig. 1), in typical polyurethane reactions; and b) preparing water-borne PUDs mainly from dimer fatty acid-based diisocyanates (DDI 1410) and IS. L-lysine diisocyanate was used as a second diisocyanate material to tune the T_g of the PU prepolymers. The petrochemical-based dimethylolpropionic acid (DMPA), neutralized with triethylamine (TEA), was used as the internal dispersing agent. These PU prepolymers were ultimately chain extended in dispersions with diamines to obtain high molecular weight poly(urethane urea) products. To characterize the resulting PU prepolymers and PUDs, ^{1}H NMR, FT-IR, SEC, titration, TGA and DSC techniques were used.



isosorbide (IS) methyl ester L-lysine diisocyanate (MELDI)

Fig. 1: the molecular structures of IS and MELDI

In this contribution, the reactivity as well as the regio-selectivity of IS and MELDI during PU reactions will be discussed, leading to a better understanding of how to control prepolymer composition and functionality. In addition, an improved procedure to prepare stable, bio-based PUDs will be presented.

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BIOSOURCED MONOMERS AND RESULTING (CO)POLYMERS: TOWARDS ORIGINAL GREENER (CO)POLYESTERS/POLYCARBONATES/POLYURETHANES

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Cyclic esters including diesters and carbonates are, for some of them, synthetically accessible from natural renewable resources such as vegetable oils or animals fats. In particular, lactide (LA) is derived from sugar cane or sugar beet, while trimethylene carbonate (TMC) is prepared from glycerol, the by-product formed during the production of biodiesel. These cyclic monomers undergo ring-opening polymerization (ROP) thereby affording poly(lactide) (PLA) and poly(trimethylene carbonate) (PTMC), respectively. The synthesis of such biosourced polyesters and polycarbonates, with solvent-free conditions, atom-economic procedures, highly efficient (in terms of both activity and productivity) catalytic systems, is presently an important endeavour given the global emphasis on sustainable materials, and considering their potential as alternatives to current petroleum derived commodity polymers. We have thus been developing the so called “immortal” ROP (iROP) of TMC under mild operating conditions including bulk reaction medium, moderate reaction temperatures, non-toxic metal catalyst, metal-free catalyst and true catalytic amount of catalyst loading. This process was successfully catalyzed by inherently different systems ranging from simple basic organocatalysts, simple Lewis acidic metallic salts such as triflates, or more sophisticated discrete metallo-organic complexes derived from oxophilic metals (typically zinc). Highly efficient catalytic systems have been unveiled, some of them being still very active and productive towards the iROP of “technical” grade TMC [1-7]. This attractive strategy has next been extended to the synthesis of other original polycarbonates, arising from new carbonate monomers, still derived from the biomass. Thus, in addition to glycerol, ethanol, 1,3-dihydroxyacetone (DHA), aspartic, levulinic or itaconic acids enabled the synthesis of six- or seven-membered cyclic carbonates and ultimately, subsequently to their iROP, of their resulting polymers. The dissymmetry of some of these monomers prompted the assessment of the regioselectivity of the catalytic system in the ring-opening of the monomer [8-11]. This route towards poly(trimethylene carbonate)s (PTMCs) further allowed access to copolymers featuring polyester segments of the PTMC and PLA type. In particular, the α,ω-dihydroxytelechelic PTMCs were also valorised towards the isocyanate-free synthesis of poly(carbonate urethane)s as Non-Isocyanate PolyUrethanes (NIPUs).[12] Our most recent results in the field of iROP of cyclic carbonates derived from biomass resources, with a variety of catalysts including metallo-organic, metallic and organic examples, highlighting their respective catalytic performance/efficiencies and overall rewards, will be exemplified.

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NOVEL CELLULOSE DERIVATIVES FOR MAKING MODIFIED POROUS CELLULOSIC MATERIALS

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Nowadays the urge to find and create new alternatives for sustainable utilisation and use of renewable materials is greater than ever. In view of these circumstances cellulose, as renewable resource, is considered a promising material which could help to provide a possible solution for this quest we are facing momentarily. The development of novel cellulosic materials with high added value is thus of great interest.

Aerocellulose, an aerogel-like highly porous and ultra-light cellulose, is a new material recently developed in our laboratory [1,2]. Aerocellulose density is 0.05-0.2 g/cm^3, with pore sizes varying from a few nanometers to a few microns and high specific surface of 200-300 cm^2/g. It is prepared via cellulose dissolution followed by coagulation and drying in supercritical CO_2. Aerocellulose applications can vary from biomedical, pharmaceutical and cosmetics to insulation and electrochemical (when pyrolysed). However, for some applications cellulose hydrophilicity may cause problems. In this work we performed the synthesis of various silica-cellulose derivatives, their properties and newly formed porous cellulosic materials.

Two ways were considered to achieve this goal. One is to perform homogeneous cellulose modification in solution and prepare new materials via coagulation and drying route. Cellulose was modified using silylation or other hydrophobizing reagents such as TMSCl or TritylCl [3-6]. The modification took place only at OH groups of the polysaccharide. The degree of substitution for the resulting products was varied by controlling reaction conditions. The second way is to directly modify aerocellulose precursor, i.e. wet coagulated cellulose. The newly obtained materials were analysed by means of IR, SEM, elemental analysis and water absorption tests.

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SYNTHESIS AND BONE TISSUE REACTION OF BONE-LIKE NANOSTRUCTURED HYDROXYAPATITE/COLLAGEN NANOCOMPOSITE

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Bone is a typical nanostructured materials in which nonstoichiometric hydroxyapatite (HAp) nanocrystals are aligned along long axis of type-I collagen (Col) molecules as well as their fibers. To realize the ultimate artificial bone material, many researchers have been trying to synthesize composite of HAp and collagen by mainly following two methods: 1) mixing of HAp and collagen and 2) deposition of HAp nanocrystals on collagen fibers. The former is very simple to prepare bone-like HAp:Col mass ratio materials but never succeeded to form bone-like nanostructure and the latter can form bone-like nanostructure in very low HAp:Col mass ratio but is very difficult to form bone-like nanostructure at high (bone-like) HAp:Col mass ratio as well as required long time to obtain bone-like HAp:Col mass ratio. In 2001, we succeeded in synthesize bone-like nanostructured HAp/Col composite with bone-like mass ratio within very short (less than an hour) synthesis time. The method is very simple that calcium hydroxide suspension and orthophosphoric acid solution with appropriate Col molecules are titrated into reaction vessel with controlled temperature and pH [1]. After our report, Olszta *et al*. succeeded in preparation of HAp nanocrystals in Col fibers, which mimics bone formation more precisely in comparison to our method, using polymer induced liquid precursor method [2]. Including this method, several synthesis methods reported in this decade are, however, not suit for mass production of materials, because time for preparation is too long and/or control method of preparation condition is too complex. Thus, bone tissue and bone-related cell reactions are almost similar in the materials obtained from above method, our method is the best for regenerative medicine.

We examined influences of the HAp/Col on osteogenic activities and osteoclast differentiation activities by cell culture tests. As a result, the porous HAp/Col enhanced osteogenic activity in comparison to Col sponge, and the HAp/Col affected on osteoclastic differentiation through activation of osteoblastic funtions as shown in Fig.1. We also examined bone tissue reactions in small size defect of SD-rats and bone tissue regeneration efficacy using critical size tibial defect of dogs. From rats' test, we confirmed that the HAp/Col was resorbed by osteoclasts followed by osteogenesis by osteoclasts, *i.e.*, the HAp/Col was incorporated into bone remodeling process as the same as transplanted autologous bone. The critical tibia defect of dogs was also regenerated completely using the HAp/Col materials. After the results, the porous HAp/Col with sponge-like viscoelasticity is now on the way to approving process of Ministry of Health, Labor and Welfare, Japan to be commercialized. In addition, we succeeded to prepare several type of HAp/Col materials such as membrane, core-shell and injectable ones. On the podium, preparation of these types of the HAp/Col will also presented.

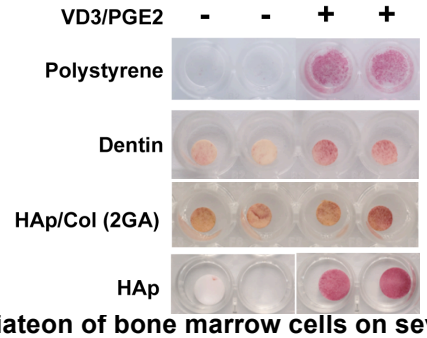

Fig. 1: Osteoclastic differentiateon of bone marrow cells on several materials. Only HAp/Col differentiated cells into osteoclasts (red stained) without supplements.

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SELECTION AND CHARACTERIZATION OF DIAMOND-LIKE CARBON BINDING PEPTIDES

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Material binding peptides have attracted great interest in nanotechnology and molecular biomimetics. They are good models for studying molecular recognition between proteins and inorganic surfaces, and also offer many possibilities for utilization in modern applications like biomimetic composite materials, biosensing, tribology, nanoelectronics, drug delivery and bioremediation. Phage display is one of the techniques used to identify such peptides. Target specific peptides are selected form the library of random peptides with different amino acid composition that is displayed on phage surface. Selected peptides can be studied by experimental and computational methods to define their sequence, structure and binding properties, subsequently engineered with the use of recombinant DNA technologies in order to improve their binding affinity and tailor their function. Selected, investigated and genetically engineered material-specific peptides can be utilized as building blocks for various nanotechnological applications that require target specific recognition.

In these studies we identified diamond-like carbon binding peptides (DLCBP) from a commercial phage display library displaying 12-mer peptides (New England Biolabs). During the selection process, phage clones displaying 42 – 57 amino acid residues were enriched in addition to clones displaying the nominal 12 residues. Long peptides are a side-product created during library generation and represent only <1% of the original library. Binding studies of selected phage clones by phage ELISA and phage titer analysis indicated that phage displaying long peptides bind more efficiently to DLC surface than phage displaying standard 12-mer peptides. Selected DLCBP were fused to bacterial alkaline phosphatase (AP) that was used as a reporter enzyme in order to determine their binding properties outside of the phage particle context. Adsorption of the DLCBP-AP fusions on DLC was quantified using the AP enzymatic activity and verified by ellipsometry. The long peptide DLCBP11(L)-AP showed the highest binding to DLC with a binding capacity of 6.8 ± 0.4 pmol/cm^2 and a K_d value of 63 ± 14 nM. The exact molecular mechanism of binding of DLCBP11(L) is for the moment still unknown. The DLCBP as AP fusion proteins have been used for the synthesis of protein nanoparticles and in friction tests with DLC surfaces.

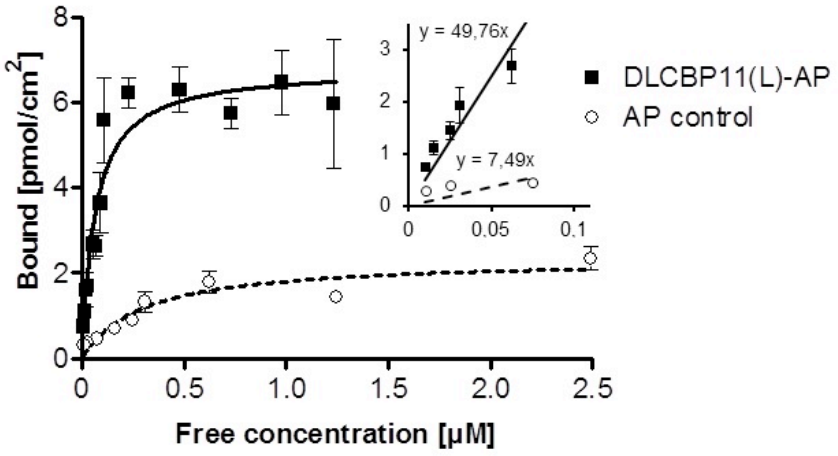

Fig. 1: Adsorption isotherms of DLCBP11(L)-AP fusion protein and AP control on DLC. Bound protein was determined by enzymatic activity and comparison to standard activity curves. The Langmuir model was fit to the adsorption data. The inset shows linear fits to the initial slopes of adsorption isotherms (as estimates of initial slopes). Data are presented as mean values and standard deviation (N=3).

A BIOINSPIRED AND ALL CONDUCTING POLYMER FOR NEURAL ENGINEERING: A INTEGRATED PLATFORM OF BIOCHEMICAL AND ELECTRICAL STIMULATION

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The neural biointerfaces are known to play a critical role in the long term efficient electrical communication between bio-electronic devices and neural tissues. Recently, the conducting polymer materials were investigated quite often as new materials for neural interfaces, as they simultaneously display the electrical characteristics of metals and the physical and chemical properties of organic polymers [1-9]. Particularly, in contrast to metal materials, the soft conducting polymers may provide an improved bionic interface between the rigid electronic devices and the soft biological systems. However, the conducting polymer materials as neural interfaces normally face immunogenic and inflammatory response in vivo once implanted in body, which largely increases the electrode impedance and leads to the loss of the intimate electrical contact with targeted cells and tissues.

Toward solving this issue, one concept, i.e., to endow the conducting polymer the capability to recognize and selectively attach the neural cells by a biomimetic approach, is provided and demonstrated in our manuscript on a molecularly-defined chemistry. The EDOT derivatives bearing the zwitterionic phosphorylcholine and conjugatable groups were synthesized as the building blocks of the targeted conducting polymer materials. The zwitterionic phosphorylcholine group is superhydrophilic and neutral, and thus anti-biofouling (protein- and cell-resistant), which could reduce the inflammatory response significantly both in vitro and in vivo. A new protocol for electro-copolymerization was developed by using inverse emulsion to copolymerize the building blocks which present diverse polarities and solubilities. Utilization of electro-copolymerization with a mixture of conjugated monomers allows very quick formation of conducting polymer films which can be then utilized for bioengineering. It finally supply us a facile access to a tunable conducting surface with various surface group densities. It is quicker, more controllable and less limited than the commonly-used post-functionalization. This work further gave the demonstration for the neuron-recognizable conducting polymer material. The neuron-recognizable selective binding was accessed by finely defining the density of neuron-targeted IKVAV ligands on zwitterionic phosphorylcholine background.

The biomimetic conducting polymer material could selectively recognize and attach the neural cells, and further support well the cell proliferation and differentiation, while persist the low impedance as the unfunctionalized EDOT polymer. The unique combination of the selective cell binding (intimate contact with targeted cells and tissues and small immunogenic and inflammatory response) and low impedance (low power electrical signal and small damage to cells and tissues) on one material actually promise its potential to supply long term efficient electrical communication between the bio-electronic devices and neural tissues. It could be spatially defined in both side-by-side and layer-by-layer ways, and potentially act as the electronic biointerfaces in the scaffold for nerve regeneration, the neuroprosthetic devices, and biosensors. To demonstrate its potential in never regeneration application, this work further carried out a simple electrical stimulation of neural cells on the biomimetic conducting polymer material, and the neurite growth could be enhanced 123.8%, which is significantly greater than those reported previously. The in vitro results support our material as one of the best platforms to electrically guide the neurite growth, even without considering its potential superiority at long term in vivo application.

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COMPUTER MODELLING OF GLUCOSE DEHYDROGENASE-BASED AMPEROMETRIC BIOSENSOR

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A number of characteristics are important in the development of actual biosensors. Mathematical models have been widely used to study and optimise analytical characteristics of the biosensors.
In this paper Glucose dehydrogenase-based amperometric biosensor that acts in a synergistic manner was modelled numerically [1-3]. The mathematical model was based on a system of non-linear reaction diffusion equations and comprised three compartments: an enzyme layer, dialysis membrane and an outer diffusion layer.
The synergistic scheme of the glucose dehydrogenase biosensor contains the step of reduced enzyme interaction with both substrates (2, 3) as well as a cross reaction of the ferricyanide and reduced mediator (4). The glucose dehydrogenase is reduced with glucose (1),

$$GDH_{ox} + glucose \xrightarrow{k_{red}} GDH_{red} + P, \quad (1)$$

$$GDH_{red} + 2F_{ox} \xrightarrow{k_f} GDH_{ox} + 2F_{red}, \quad (2)$$

$$GDH_{red} + 2M_{ox} \xrightarrow{k_{ox}} GDH_{ox} + 2M_{red}, \quad (3)$$

$$F_{ox} + M_{red} \underset{k_{ex(r)}}{\overset{k_{ex(d)}}{\rightleftharpoons}} F_{red} + M_{ox}, \quad (4)$$

where GDH_{ox} and GDH_{red} are the oxidized and reduced glucose dehydrogenase, *P*-reaction product (*δ-glucolactone*), F_{ox} and F_{red} – ferricyanide and ferrocyanide, M_{ox} and M_{red} stand for oxidized and reduced mediators, respectively. The constants k_{red}, k_f and k_{ox} correspond to respective biocatalytical process, $k_{ex(d)}$ and $k_{ex(r)}$ refer to the forward and reverse synergistic reaction, respectively.
Both, the mediators and hexacyanoferrates are redox active compounds (5, 6). Therefore, the biocatalytical current is produced during ferrocyanide and mediator oxidation,

$$F_{red} - e^- \rightarrow F_{ox}, \quad (5)$$

$$M_{red} - e^- \rightarrow M_{ox}. \quad (6)$$

The numerical simulation using finite difference technique was employed to solve the stated problem. The program was implemented in Java programming language.
By changing input parameters the biosensor response and sensitivity were analysed with a special emphasis on the synergy of the simultaneous substrates conversion. The adequacy of the computer model of the biosensor was evaluated by using the obtained experimental data [2].

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ADHESION BEHAVIOUR OF CELLS ON CERIUM OXIDE NANOPARTICLE LAYERS WITH STABLE TRIVALENT IONS

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Development of scaffold design and medical applications using artificial materials requires a better understanding of the interactions between a living cell and a matrix. Cell interactions with materials such as ECM and scaffolds induce intracellular reactions, resulting in better adhesion, spreading and proliferation. For instance, the promotion of cell proliferation by a cerium oxide (ceria) nanoparticle dispersed composite-scaffold has been reported [1]. Furthermore, ceria nanoparticles were found on the scavenging activity of ROS (reactive oxygen species) related to redox reactions that can reversibly convert the Ce^{4+} into the Ce^{3+} oxidation state. The mixed-valence-state ceria nanoparticles have the capability to scavenge toxic reactive oxygen intermediates (ROIs), inhibiting the progression of ROI-induced cell death and showing therapeutic potential [2]. The cellular antioxidant and anti-apoptotic effects of ceria nanoparticles are due to the presence of Ce^{3+}/Ce^{4+} redox couples in ceria nanoparticles [3]. The reversible cycles between Ce^{3+} and Ce^{4+} allow ceria nanoparticles to react catalytically with superoxide and hydrogen peroxide, mimicking the behavior of superoxide dismutase (SOD) and catalase enzymes, respectively [4]. However, the mechanism of the interaction between ceria nanoparticles and cells is still unclear. In this research, stable and high concentration of Ce^{3+} ions were created in the ceria nanoparticle layers on a biodegradative polymer used as scaffold material. Our findings indicated that the adhesion behavior of cells on the ceria nanoparticle layers differed significantly according to valence states. To better understand this interaction mechanism, we controlled Ce^{3+}/Ce^{4+} ratios to reveal the valence effect on cell functions. This presentation discusses physiological functions of the adherent cells on the ceria nanoparticle layers in different valence states, e.g. cell proliferation and cell cycles.

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PEPTIDE NANOSTRUCTURES FUNCTIONALIZED WITH HYPERICIN

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Hypericin (Hyp) is a natural pigment found in plants of the species of Hypericum (St. John wort). Its high ability to form singlet oxygen ($^1O_2$) makes the molecule suitable for applications in photodynamic therapy (PDT) for treatment of tumors and other cellular degenerations.[1] In this study, peptide nanotubes (PNTs) were functionalized with Hyp (λ_{em} = 590 nm) to study their potential application in PDT. By using the liquid-phase approach, the tubes were self-assembled and functionalized with Hyp at concentrations ranging from 0.65 to 9.94 μmol L^{-1}.[1] The diameters of the tubes are found to be of the order of 320 nm. X-ray diffraction show that the symmetry of the molecular arrangement belongs to the space group *P61*. Interestingly, we observe that the lattice parameter *c* increases upon the addition of Hyp. To assess the interaction of the Hyp with the PNTs, we carried out some MD simulations (insert in Fig. 1), which point the intercalation of the fluorophore into the peptidic matrix. This result is corroborated by fluorescence and SEM images. The generation of reactive oxygen species (ROS) in the functionalized materials was studied via UV / Vis spectroscopy. For this, we used an indirect method employing 1,3-diphenylisobenzofuran (DPBF). This molecule reacts with 1SO (generated by the excitation of Hyp) forming an endoperoxide. The reaction occurs as the absorbance of DPBF (λ_{exc} = 417 nm) decreases, enabling the measure of the speed of singlet generation. In Fig. 1, we show the behavior of 1SO production as a function of the Hyp concentration either for bare Hyp or PNTs + Hyp. We observe that the production of 1SO is ~25 % faster for PNTs+Hyp. Lifetime measurements reveal that the introduction of peptidic structures also increases the endurance of the reactive species (4.8 ns for PNTs + Hyp and 2.7 ns for bare Hyp). These results highlight the efficiency of PNTs in the generation of ROS and demonstrate the potential of these structures for PDT applications.

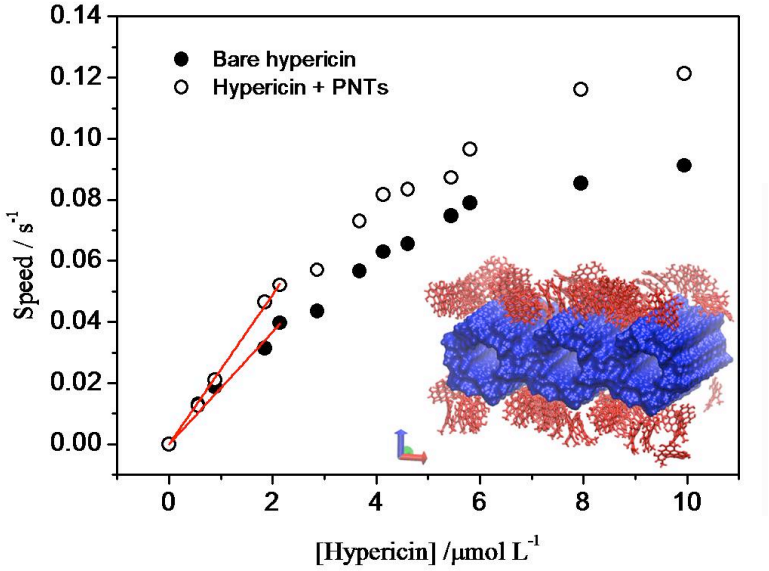

Fig. 1: Speed of production of singlet oxygen as a function of hypericin concentration for naked hypericin and peptide nanotubes containing hypericin (inset).

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RING-OPENING POLYMERIZATION OF HETEROCYCLES USING ORGANOMETALLIC COMPLEXES: A SIMPLE ACCESS TO BIODEGRADABLE POLYMERS

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There are economic and social issues associated with the depletion of fossil feedstocks and the accumulation of conventional polyolefin plastics. Given the growing need for inexpensive biodegradable plastics for use in various applications, the development of synthetic methods for the polymerization of a wide range of monomers with control over the stereochemistry, molecular weight, and comonomer incorporation is of particular importance [1].

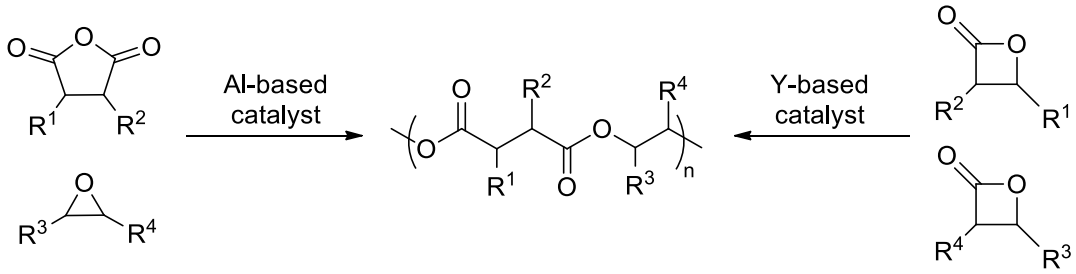

Fig. 1: Synthetic approaches to aliphatic polyesters

In this context aliphatic polyesters have emerged as biodegradable materials with huge potential. Recently we have synthesized new biodegradable poly(β-hydroxyalkanoate)s (PHAs) with controlled primary structures [2]. By using highly efficient yttrium complexes as initiators, we were able to synthesize highly alternating copolymers by ring-opening polymerization of a mixture of enantiomerically-pure but different monomers. This efficient catalytic system makes copolymers that would be very difficult to make through any other method. Also we have reported a new strategy to obtain biodegradable polyesters [3]. This was achieved by tandem catalysis, which confers great interest to this approach. Commercially available complexes were used as efficient catalysts for cyclization of dicarboxylic acids followed by alternating copolymerization of the resulting anhydrides with epoxides. Given an operationally simple method, this tandem catalysis is an attractive strategy for the production of new renewable materials.

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INVESTIGATION OF MODIFIED ACTIVATED CARBON CHARACTERISTICS BY ADSORPTION METHODS

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Moscow State University of Fine Chemical Technologies named after M.V. Lomonosov

It has been shown [1-3] that the oxidation of activated carbons (AC) by nitric acid highly influences their adsorption capacity as to benzene, acetic acid and salt catalysts. The $Zn(OAc)_2$/C supported AC catalysts exceed in activity the "Montecatini" MAVC catalyst [3], one of the best in vinylacetate synthesis.

The investigations of other ways of AC surface modification (AC treatment by acetic acid and H_2O_2) have demonstrated that obtained AC to have boath an increased adsorption capacity as to $Zn(OAc)_2$, optimum volumes of meso- and micropores and high catalyst activity in vinyl acetate (VA) synthesis [2]. The results of these investigations are given below.

The characteristics of supports were found out by benzene, ethanol, water and acetic acid vapours adsorption by means of vacuum adsorption laboratory installation with McBen scales, under initial pressures of 10^{-4} – 10^{-6} torr at temperature 25 ^{o}C.

Modified sorbents characteristic properties.

The AGN-2 AC porous structure after H_2O_2 treatment (AGN-2K) changed greater than after AcOH (AGN-2U) treatment. The mesopores volume increased by approx. 25%, the specific surface area value of AGN-2K increased by 40 m^2/g reaching 910±10 m^2/g. By AC oxidation the partial decarboxylation takes place. Judging by the results of elemental analysis on C and H of oxidized carbons (AGN-2) by H_2O_2, H/C ratio after carbons treatment with H_2O_2 increases from 0,35 to 0,52, the adsorption capacity as to water, ethanol and benzene increasing as well.

On the oxidized AC the number of available adsorption sites on both polar (H_2O, CH_3COOH) and non-polar (benzene) compounds as well as the adsorption capacity (*a)* increased by 25-30%.

However, at full surface pores filling (P/Ps=0.8) the (*a)* value of benzene increased by 14%, and that of water – by 36%, the heat of water adsorption λ_{H2O} increased by 58 kJ/mole, and that of benzene – approx. by 7 kJ/mole (Table1):

Table 1: Dependence of adsorption heat on methods and treatment of activated carbon

Sample AC	λ_{C6H6} (kJ·mole^{-1})	λ_{H2O} (kJ·mole^{-1})
AGN-2	53.5	40.1
AGN-2K	60.6	98.2

Adsorption capacity (on oxidized surface AGN-2 with H_2O_2) as to AcOH rises sharply as is shown on. The relatively higher growth of surface polarity (hydrophilicity) is also confirmed by adsorption capacity increase as to methylene blue (2.5 times approx.). These changes of surface properties (together with mesopores volume increase) became apparent in growing of adsorption capacity as to zinc acetate [3]. AC, treated by AcOH, changed its porous structure slightly as shown by adsorption measurement results, though that part of supermicropores with radius of approx. 5Å *(as of according)* to SAXS measurements increased by approx. 40%. The minor expanding of mesopores caused by removal of impurities and small quantity of resins left after activation can be observed (the third peak on fig.3) as well.

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DEVELOPMENT OF HIGH-PERFORMANCE POLY(LACTIC ACID)S

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Bio-based polymers include naturally occurring polymers with and without chemical modification, the polymers chemically synthesized from various naturally occurring resources and those synthesized by microorganisms.
Among these bio-based polymers, thermoplastic aliphatic polyester such as poly(lactic acid) has been attracting much industrial attention. However this polymer has its intrinsic problems which may be a major obstacle to the practical applications
In this paper, the development of thermally resistant poly(lactic acid) fibers and the control of the crystallization behavior and the melt-rheology by utilizing the stereocomplexation phenomenon are presented.

Development of Thermally Resistant Poly(lactic acid) Fibers

Since the poly(l-lactic acid) (PLLA) is a thermoplastic polyester, the conventional melt-processing technology can be applied to manufacture various products with a good mechanical property. One of the problems, which may be a major obstacle to the practical applications of PLLA, is its low thermal resistance, especially when it is to be used as textile fibers. The fundamental solution to this problem may be a utilization of the high-melting point stereocomplex (SC) which forms in the equal blend of PLLA and poly(D-lactic acid) (PDLA).
The thermally resistant fiber consisting of the SC crystal was successfully obtained by two different approaches. One of them is to melt-spin the PLLA/PDLA equal blend following a special melt blending process. The other is to melt-spin the block co-polymer of L- and D-lactic acids (stereo-block PLA, sb-PLA). In both cases, the fibers drawn to several times have a smectic structure which immediately transforms into SC completely during annealing process in few seconds.

Control of the Crystallization Behavior of Poly(lactic acid)

It has been known that the poly(L-lactic acid) has a very low crystallization rate. This limits the productivity in the Injection molding process and various crystallization nucleating agents have been developed. Poly(D-lactic acid) (PDLA), an enantiomer of PLLA, can be an effective nucleating agent.
The addition of small amount of the PDLA produces the SC crystallites dispersing in the PLLA matrix. Since SC has a higher melting temperature than PLLA homo-chiral crystal (HC), SC crystallites can stay as solid even at a melting state of PLLA. The nucleation rate and the crystal growth rate are significantly enhanced especially when only 1wt% of the high Mw PDLA is added. However the addition of higher amount of PDLA reduces the crystallization rate due to the formation of a network structure.

Control of Melt-rheology of Poly(lactic acid)

Poly(lactic acid) is a linear polymer with a fairly narrow MWD, Mw/Mn ~ 2.0. Because of this molecular characteristics, the melt tends to be stable in a high uniaxial extensional flow and suitable for melt-spinning process. However this sort of rheology may not be suitable for the other processing operations.The addition of D-lactic acid chain into PLLA does not only affect the crystallization behavior, also control the melt rheology of PLLA. The addition of the high Mw PDLA into PLLA produces the SC crystallites which act as crosslinking points of PLLA chains. The effects of the addition of the D-lactic acid chain on the melt-rheology of PLLA were studied.
The PDLA chains dispersed in the PLLA matrix act as crosslinking points and some of the PLLA chains are connected at these crosslinking points resulting in the weak network structure and the apparent molecular weight increase. Due to the change in the molecular architecture of the PLLA, the viscosity and the elasticity in shear flow increase and the strain hardening behavior in the extensional flow is enhanced. On the other hand, the addition of sb-PLA with a short D-chain (long L-chain) does not affect either the viscosity or the elasticity and only the strain hardening behavior in extensional flow is enhanced.
Various molecular architectures may be designed utilizing the stereocomplexation phenomenon without modifying the chemical structure. One can make a choice of the melt-rheology suitable for the individual processing operation.

CO_2 AS NICE RAW MATERIAL: SELECTIVE SYNTHESIS OF CYCLIC CARBONATES

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Carbon dioxide is a nice raw material, since it is largely available, cheap and easy to handle. Even if some large scale processes already uses CO2 as a renewable carbon source [1], the study of other « moderate CO2 amounts » reactions can be interesting from a sustainable point of view, as for example the organic carbonates synthesis from the CO2 addition to alcohols or epoxides. Organic carbonates can be linear, cyclic or polymeric, all of them having interesting properties and various uses, mainly as biodegradable solvents and plastics having sustainable properties. Starting from epoxides, the insertion of CO2 can lead to cyclic carbonates or polycarbonates (figure 1), the reaction selectivity being a challenge.

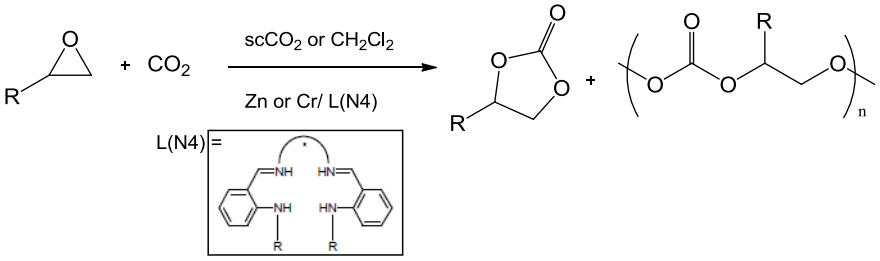

Fig. 1: Carbonate synthesis by CO_2 insertion to epoxides

Homogeneous catalysts can be used for this reaction, using complexes with different metals (Al, Cr, Mn, Co, Zn) and ligands, such as porphyrins and Salens [2-4] . Both type of nitrogen ligands (N_2O_2 or N_4) inspired us to use other N_4 Schiff bases [5] (figure 1) to prepare a series of complexes as potential catalysts for the CO_2/epoxide insertion. Various metals were used to synthesize a series of complexes and their catalytic activity was tested on the addition of CO_2 to styrene oxide. Better cyclic carbonate selectivity was obtained with Zn-N_4 complexes, while Cr-N_4 complexes favoured the polycarbonate synthesis.
This reaction was carried out in classical organic solvents to optimize the reaction conditions and extend it to other epoxides. Under supercritical conditions, CO_2 could be used as both, the substrate and the solvent, leading to improved rates and selectivities. This presentation will browse our main results and show how the reaction can be tuned to the cyclic or the polymeric carbonates.

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SYNTHESIS OF ISOSORBIDE BASED POLYURETHANES: AN ISOCYANATE FREE METHOD

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Generally, linear polyurethanes (PUs) are obtained from the reaction of an oligomeric polyol (low molecular weight polymer with terminal hydroxyl groups) and a diisocyanate plus a short diol as chain extender. To prepare cross-linked PU, polyols or isocyanates with functionality higher than 2 can be used. However the use of isocyanate reactants should be avoided for several reasons (harmful for human health, precursor phosgene, etc.).
Therefore the synthesis of PUs from step growth polyaddition of dicyclocarbonates and diamines should be favoured [1,2]. Thus, this old reaction is currently gaining a lot of attention as a substitution route for the synthesis of Pus.
Isosorbide is obtained from the dehydration of sorbitol, which is a product of the sugar industry. Its structure is composed of two secondary hydroxyl groups. Isosorbide is a platform chemical extensively studied in literature with various industrial applications (isosorbide nitrate, diesters, lubricants and plasticizers, green solvents, etc.) [3,4]. It has to be noticed that the synthesis of the corresponding isosorbide amine and isocyanate was also reported [5,6]. Applications of isosorbide in polymers and materials are even more important and are summarized in the Fig. 1.

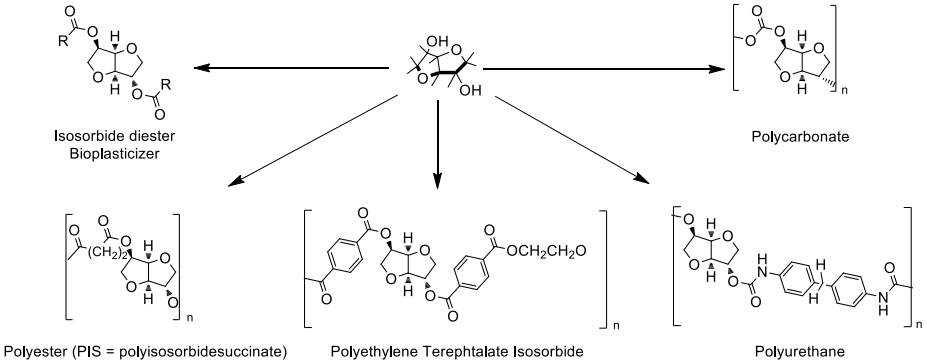

Fig. 1: Applications of isosorbide.

This work aims to prepare isosorbide based polyurethanes without isocyanate owing to the carbonate-amine chemistry. The first step of the synthesis is the epoxydation of isosorbide followed by a carbonatation reaction. Carbonatation is simple, easy and provides the corresponding dicyclocarbonates with high yields. Thern isosorbide dicyclocarbonates and their corresponding PHUs have been synthesized by a new, easy and inexpensive method with high conversions [7]. This method involves the reaction of a cyclocarbonated isosorbide and various diamines at low temperature. These materials are able to be used as coatings owing to their T_g and T_d close to 0 °C and 240°C respectively. To the best of our knowledge, no paper or even patent claims the synthesis of these new and green PHUs.

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AEROCELLULOSE: AN ULTRA-LIGHT AND POROUS CELLULOSE. INFLUENCE OF PROCESSING PARAMETERS ON FINE MORPHOLOGY

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Highly porous materials and aerogels are of special interest in a wide range of applications from pharmaceutical and cosmetics to heterogeneous catalysis and insulation. Cellulose is one of the most abundant natural polymers on Earth and promising candidate for the development of novel environmentally friendly bio-based materials. One way to prepare highly porous cellulose-based materials, called "Aerocellulose" [1], is inspired by aerogel preparation route: cellulose is first dissolved in a solvent then coagulated in a non-solvent and finally dried in supercritical CO_2 to avoid pores collapsing and keep the porous structure.

To prepare aerocellulose, we use cellulose "green" solvents: aqueous 8%NaOH and ionic liquid such as 1-ethyl-3-methylimidazolium (EMIMAc) [2], without and with co-solvents (dimethylsulfoxide, DMSO). Cellulose solutions in NaOH-water are gelling undergoing a micro-phase separation; aerocellulose is thus obtained from a pre-gelled cellulose. In ionic liquid, cellulose is directly coagulated from solution. DMSO, added to ionic liquid, allows to significantly decrease solvent viscosity and price and make easier aerocellulose preparation.

Depending on the preparation route, various aerocellulose morphologies are obtained: a net-like from aqueous NaOH (Figure 1a) and made of "hairy beads" from ionic liquid route (Figure 1b, c). The influence of cellulose concentration, solvent (NaOH-water or ionic liquid), type of non-solvent (water or ethanol) on aerocellulose density, porosity and morphology (specific surface area, pores size and wall thickness) will be presented and discussed.

Bulk and skeletal densities are determined with mercury and helium pycnometry, respectively. The skeletal density is independent on cellulose concentration and the nature of the solvent and co-solvent. The bulk density increases with the cellulose concentration increase and evolves with the nature of the solvents and co-solvents. To evaluate the solid part of the ultraporous materials, we used SAXS and USAXS techniques. We determined the fractal dimension for each aerocellulose and demonstrated that the particules have an homogeneous density (q^{-4} slope in the Porod zone).

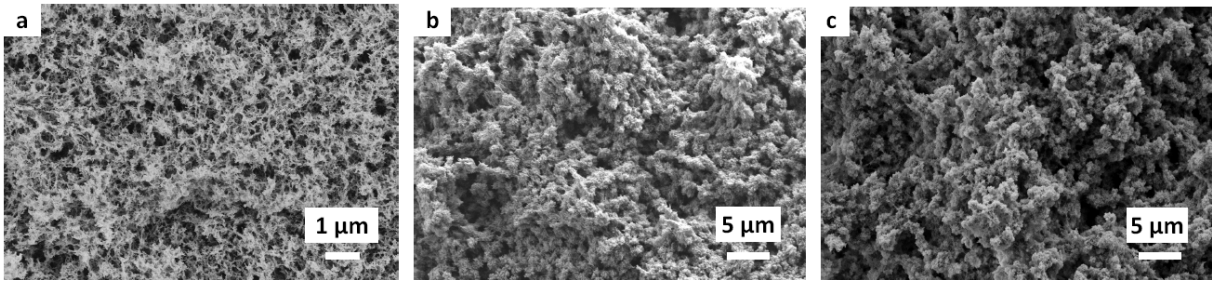

Fig. 1: SEM images of Aerocellulose prepared from 8%NaOH-water (a), EMIMAc (b) and EMIMAC/DMSO (c)

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MICRO-MANUFACTURING CELLULOSE WHISKERS / MALEIC ANHYDRIDE ENGINEERED SURFACES WITH PLASMA POLYMERIZATION

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In recent years plasma polymerization has attracted scientific interest as an environmentally friendly approach for producing micro- or nano- structured ultra-thin films. Such films are of particular interest for application in MEMS due to the possibility to manipulate topography, wettability and adhesion properties.
In plasma polymerization, maleic anhydride (MA) is one of the most studied precursors due to its high reactivity, with an insaturation as well as reactive anhydride ring. For MA polymerization, pulsed plasma allows good control of the film structure and composition even with preserved anhydride ring structures [1-3]. At the same time, cellulose nanofibers in the form of whiskers of MFC have also started a “revolution” in the field of bio-based materials opening new avenues for the design of materials at the nano-scale.
In this work, a new approach for the development of engineered surfaces is proposed based on the production of model nanocellulosic surfaces followed by MA plasma polymerization. In contrast to some of our previous work where buckled surfaces could be prepared [4,5], new methods produced surfaces with different topological designs depending on the parameters used. This work further asserts that plasma polymerization is a promising technology for micro-manufacturing surfaces and composites based on cellulose nanofibers.

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NEW ENVIRONMENTALLY FRIENDLY METHOD TO EFFICIENTLY EXTRACT CELLULOSE NANOWHISKERS

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Cellulose nanowhiskers (CNWs) are commonly used as a reinforcing material due to their high aspect ratio and stiffness. Acid-catalysed hydrolysis reaction is the main method proposed to produce CNWs from cellulose fibres at elevated temperature [1-3]; yet the use of tixic chemicals is not very environmentally friendly [4].
In this presentation we will propose an environmentally friendly method to produce CNWs under a much milder acidic conditions in high yield. Transmission electron microscopy (TEM), atomic force microscopy (AFM) were employed to characterize the morphology and dimensions of the nanowhiskers, while Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD) were used to analyze their chemical structure and crystallinity. Furthermore, Ekenstam equation [5] was applied on the kinetics study to clarify the degradation evolution with different regimes from wood pulp to nano-sized fibers under different conditions. The acid (H^+) to anhydroglucose molar ratio used in the reaction was calculated and compared with the traditional CNWs production method that used concentrated sulphuric acid. We propose that this method might be a better choice to the actual production of CNWs.

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STUDY OF INTERACTIONS BETWEEN OCTHYL-β-D-GLUCOPYRANOSIDE AND THE BIOPOLYMER HIDROXYETHYLCELLULOSE IN DRUG DELIVERY

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Concentrations CMC (critical micelle concentration), C_2 (saturation concentration) and C.A.C (critical aggregation concentration), and thermodynamic parameters (ΔH, ΔG y $T\Delta S$) were determined from aqueous mixtures of octhyl-β-D-glucopyranoside and a biopolymer of cellulose (hidroxyethylcellulose) in order to design a phase diagram to study the interactions in each region and choose the appropriate carrier for using in drug delivery.

Posters Abstracts

PHYSICO-CHEMICAL CHARACTERIZATION OF ALGERIAN MINERAL FIBERS: ACID ACTIVATION

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The object of this work is to study the physico-chemical properties of Algerian palygorskite minerals fibers, used as a basis for preparing nanocomposites and catalysts. This phyllosilicate is an important clay mineral with many industrial applications, due to its fibrous nature, colloidal and sorption properties.
In the first time, the attapulgite is a rock, but after crushing the clay, it becomes a powder called Atta@dz. The Atta@dz was characterized by different methods as: Chemical analysis, X ray diffraction, Infrared spectra, BET surface, Mössbauer spectroscopy, environmental scanning electron microscopy, thermals analyses ATD-ATG and MAS-NMR methods. The first analyses shows that the total chemical composition is: SiO_2-37.45; Al_2O_3-7.34; MgO-9.86; Na_2O-0.13; Fe_2O_3-3.20; CaO-12.20; K_2O-0.79; TiO_2-0.46, a d-spacing of 10.27 Å, with existence of the corresponding peaks to calcite, critobalite, quartz and a specific surface of 80 m^2g^{-1}. All this allowed us to confirm that our clay is a carbonate attapulgite riche of aluminum.
In the second time, the acid treatment of the atta@dz for different concentrations is studied in order to eliminate impurities. The XRD spectrum of the atta@dz treated with acid demonstrated there is no destruction of the octahedral sites accompanied by the disappearance of the calcite peak.

CHEMICAL COMPOSITION AND BIOLOGICAL ACTIVITIES OF *NIGELLA SATIVA* VOLATILE OIL ISOLATED BY MICROWAVE STEAM DISTILLATION USING THE CRYOGRINDING

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Keywords: *Nigella sativa,* Ranunculaceae, composition, Microwave, Steam-distillation, Cryogrinding, GC and GC-MS, Antimicrobial activity, Antioxidant activity.

The volatile oils of Algerian *Nigella sativa* seeds, extracted by steam distillation assisted by microwave [1-3] using the cryogenic grinding (CG) were analyzed by GC, GC-MS. According to the data values reported in this study the effect of cryogrinding on the chemical composition of the volatiles is important. Monoterpene hydrocarbons (51.2-60.2%) were the main group of CG volatiles compared to SG (classical grinding) volatiles (33.3-47.8%). Whereas, the ketones formed the main proportion in SG volatiles (46.1-59.9%) followed by CG volatile oils (32.7-40.8%).
Forty-nine compounds were identified and significant differences in quantities of the major constituents were observed, mainly were thymoquinone (SG: 42.3-56.1% and CG: 28.1-36.0%) *p*-cymene (SG: 23.2-31.5 %, CG: 33.0- 38.0%), dehydro-sabina ketone (SG: 3.1- 3.3%, GC: 4.4-4.5%), carvacrol (SG: 1.3-1.4%, CG: 0.4-1.1%) and longifolene (SG: 1.5-2.1%, CG:1.3-1.7% respectively).
Moreover, *Nigella S*. Volatile oils exhibited higher antibacterial and antifungal activities varying according to technique extraction and grinding mode used, with a high effectiveness against Gram-positive bacteria with a diameter of inhibition zones growth ranging from 9.5 to 35 mm and MIC and MBC values ranging from (0.042–0.10 mg/ml) to (0.20–0.75 mg/ml), respectively.
On the other hand, the *Nigella sativa* volatile oil was investigated for its antioxidant activities using four different tests then compared with BHT. Results showed that *Nigella S.* volatile oil exhibit a good activity in each antioxidant system with a special attention for β-carotene bleaching test (IC50: 19 to 28 µg/ml) and reducing power (EC50: 8 to 15 µlg/ml).

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CONTRIBUTION TO THERMODYNAMIC AND KINETIC INVESTIGATIONS OF Pb^{2+} ADSORPTION ONTO ACID-ACTIVATED CLAY

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Keywords: Acid-activated clay (AAC), Removal, wastewater, Pb^{2+}, Cd^{2+}.

A sample of **clay** from Maghnia (N.W. Algeria) was chemically treated and characterized by powder X-ray diffraction, FT-IR spectroscopy and elemental analysis. The acid-activated clay (AAC) was used as adsorbent for Pb^{2+}ions from aqueous solutions by mean of batch experiments. The kinetic process was tested by applying pseudo-first order and pseudo-scond order. The classic Langmuir and Freundlich sorption models and a dual-mode approach have been tested to study the sorption of Pb^{2+}onto AAC. Thermodynamic parameters (ΔH_0 = -7.22 kJ/mol; ΔG_0 = -13.42 kJ/mol) showed the adsorption of an exothermic process and spontaneous nature, respectively. Additional studies indicated that the acid-activated clay (AAC) selectively sorbed Pb^{2+} ions in the presence of competing ions Cd^{2+}.

CONTRIBUTION TO KINETIC INVESTIGATIONS OF Cd^{2+}, Pb^{2+} Co^{2+} AND Ni^{2+} ADSORPTION ONTO ACID-ACTIVATED CLAY

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Keywords: Acid-activated clay (AAC), Removal, wastewater, Pb^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}.

A sample of clay from Maghnia (N.W. Algeria) was chemically treated and characterized by powder X-ray diffraction, FT-IR spectroscopy and elemental analysis. The acid-activated clay (AAC) was used as adsorbent for of Cd^{2+}, Pb^{2+} Co^{2+} and Ni^{2+} ions from aqueous solutions by mean of batch experiments. The kinetic process was tested by applying pseudo-first order and pseudo-scond order. Additional studies indicated that the acid-activated clay (AAC) selectively sorbed Pb^{2+} and Co^{2+} ions in the presence of competing ions Cd^{2+}.and Ni^{2+}, respectively.

THE GIBBS FREE ENERGY MINIMIZATION METHOD APPLIED TO THE COAL PYROLYSIS

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In the search for technological innovation to use coal highlights the thermochemical route consisting of the decomposition of coal by temperature, in order to generate chemical products with higher added value. The pyrolysis is a thermal decomposition which occurs with minimal or complete absence of oxygen. During pyrolysis is generated a large number of components and simultaneous reactions, making the calculation of traditional equilibrium composition, based on the determination of the equilibrium constant, complex and tedious. For this complicated problem, involving dissociation, recombination and elementary reactions is proposed a method based on the minimization of Gibbs free energy using a commercial simulator that uses the method of Lagrange multipliers for optimization. For this model, only the flow rate, the initial conditions of feed and product components are specified and details of the reaction and the equilibrium constant are not required for calculating the equilibrium composition.It took two reactors in series: the first to make the decomposition of coal where the products of the reaction are the constituents of coal in its elemental form (C, N_2, O_2, H_2, H_2O, and ashes), obtained through the elemental and ultimate analyses; the second reactor is the pyrolysis reactor based on the method of minimization of the Gibbs free energy. The reactors are followed by a flash separator for separating liquid and gaseous phases. The effect of reaction temperature (250 to 750° C) about the product yield and the equilibrium composition was studied. Were simulated 1000 kg/h of mineral coal originating in Candiota mine in Brazil and the results showed the formation of three phases throughout the temperature range studied and in medium proportions of 49% (m / m) of gas, 7% (m / m) of liquid and 44% (m / m) of ash. The main products obtained in the gas phase are carbon monoxide, carbon dioxide, hydrogen sulfide, carbonyl sulfide and methane, the solid phase was considered 100% ash and the liquid phase yielded a pyro-oil containing phenanthrene and traces of benzene and toluene. Increasing temperature favoured the production of carbon monoxide and carbon dioxide decreased as a consequence of the biggest break of the chemical bonds to produce smaller molecules. The CO_2 concentration was higher than that of CO until 650° C, with an inversion above this temperature. The methane concentration has increased with increasing temperature of pyrolysis. The hydrogen sulfide production presented practically constant during the temperature range studied, being higher than that of Carbonyl sulfide until approximately 700° C, above which the reverse behavior occurs. The simulation showed complete removal of the ashes and tar, which are the main components that pollute the pyrolysis gas, showing that the pyrolysis can be used as pretreatment for gasification.

PRODUCTION OF POLYHYDROXYCARBOXYLIC ACIDS FROM POLYSACCHARIDES

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The production of chemicals and materials from biomass is gaining in interest. Among the different options, is the metal-catalysed oxidation of polysaccharides. Studies have been conducted to use an environmentally oxidant in combination with an easily accessible transition metal catalyst. Iron or copper salts (0.01–0.1 wt. %) associated with H_2O_2 have led to oxidized starch in up to 90-99% yield, but with low carbonyl and carboxyl contents (0.04 mol CO/100g, 0.009 mol CO_2H/100g). [1] Compounds having both carboxylic and carbonyl groups (0.05 mol CO/100g, 0.024 mol CO_2H/100g) have been obtained with only 0.0039 mol% of iron phthalocyanine.[2]

We have reinvestigated the use of Fenton-type reagents for the oxidation of polysaccharides, and observed that the oxidation of starch, xylans, potato flesh and wheat flour by H_2O_2, in the presence of MSO_4 (M = Cu, Fe) as catalyst, led to depolymerization, and formation of solutions containing polyhydroxycarboxylic acids. We will discuss the influence of the oxidized compounds, which facilitate the process, leading to an efficient transformation, even with very low amounts of the catalyst. [3] The impact of photo-Fenton reaction on the yield of oxidized compounds and our recent progresses towards the use of lower amounts of H_2O_2 will be also presented.

MSO_4 (0.00004-0.001 wt.%)
H_2O_2 (100 wt.%)
M = Cu, Fe

Aqueous solutions of carboxylic acids
up to 0.62 mol CO_2H/100g of product

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SYNTHESIS OF SUBSTITUTED HEMICELLULOSE FOR PAPER APPLICATIONS

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Hemicelluloses are the second most abundant natural polymer in vegetable world after cellulose, representing 15% to 35% of plants and wood. Today, they are essentially used in their native state, for their gelling and thickening properties. Chemical modifications, including cationisation or esterification, could offer a larger range of applications in paper-making, cosmetic or food-industries.
Cationic xylan was prepared by reacting commercial xylan and 2,3-epoxypropyltrimethylammonium chloride (ETA) in the presence of base. After reaction, ethanol was added dropwise under stirring to precipitate the cationised hemicelluloses.
Xylan acetate was prepared from xylan and acetic anhydride in the presence of methanesulfonic acid. After reaction, the mixture was poured into ethanol. After work up the dry products were characterized by ^{1}H NMR spectroscopy to determine their degree of substitution (DS) and the yields were calculated from the mass.
The cationisation of xylan hemicellulose types, isolated from birchwood, was investigated with ETA as reagent [1]. The influence of reactional parameters was studied systematically and DS values from 0.1 to 1.3 were obtained with corresponding mass yields varied from 40 to 80% of recovered hemicelluloses. The hemicellulose concentration and the epoxide amount strongly affected the DS.
The esterification of xylan was also carried out in the absence of organic solvent and using methanesulfonic acid as catalyst. The reaction was optimized through an experimental design to identify the significant factors and their interactions. The optimization of reaction parameters allowed obtaining a high DS (1.6) with a maximal yield (85%) [2].

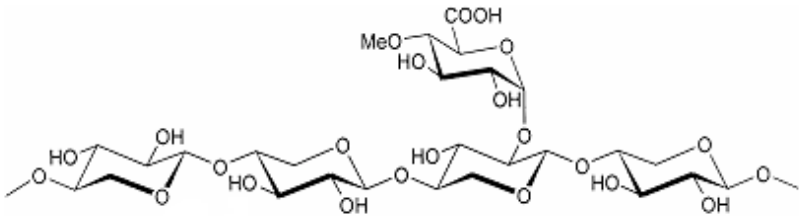

Figure 1: Structure of xylan extracted from birchwood

These modified hemicelluloses were evaluated in paper applications and some mechanical properties were improved.

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CELLULOSE CONVERSION INTO HYDROXYMETHYLFURFURAL (HMF): CATALYSIS UNDER SUSTAINABLE CONDITIONS IN AQUEOUS MEDIA

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The growing cost of petroleum and its derivatives and the progressive reduction of resources, are pushing the interest about biorefineries and green processes. A new chemistry is under development that aims at developing new catalytic reactions that transform renewable feedstock into chemicals and fuels that may substitute those usually obtained from petroleum. An example of an important intermediate obtainable form biomass is 5-Hydroxymethylfurfural (HMF) which can be prepared by dehydration of saccharides. HMF is known as a starting material in a possible production of biomass-derived fuels as well as a key platform compound for non-petroleum derived chemicals. One of its derivatives, 2,5-furandicarboxylic acid, may replace terephthalic acid as a monomer in the preparation of plastics. The most convenient synthetic method of HMF is based on the acid-catalyzed triple dehydration of fructose, and many types of acid catalysts have been used in this process, such as mineral acids, strong acid cation exchange resins, and H-form zeolites[1].
Although *"there is an abundant amount of literature available on HMF (over 1000 references), ..."*[2] the conversion of fructose into HMF with heterogeneous catalysts is not fully understood and documented. Heterogeneous acid catalysts offer the advantage of a very easy separation from the reaction products and recycle, thus appearing the most suitable catalysts for a potential industrial process.
The direct conversion of cellulose into HMF is possible working at high temperature (250°C) and using only water as solvent, but the harsh conditions required and the low stability of starting and final organic matter, lower the yield because of a high loss of material.
Our aim is to avoid the use of organic solvents (and ionic liquids), mineral acids and every poisoning-metals (frequently used in the last years), working under heterogeneous catalysis in water, in the mildest possible conditions avoiding any loss of starting cellulose as humins or any other by-products.
Here we discuss the use of mixed oxides in the catalytic reactions presented above.

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CONCEPT OF BIOMIMETIC CONTAINER OF CORROSION INHIBITORS IN PAINTS BASED ON NATURAL CLAYS

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In soils, clays particles are considered as tanks of many nutrients as calcium, magnesium, potassium cations or other molecules. This characteristic is due to their small size (at least 1000 times more external surface area than coarse sand), and to their ability to absorb positively charged ions in their bi-dimensional crystallographic structure by an exchange mechanism. This cation exchange capacity (CEC) of clays explains that soils with high CEC holds more nutrients and loses fewer of them when rainfall leaches through the soil.
The idea is to develop a novel corrosion inhibitor system based in paints based on natural clays. To mimics the behaviour of clays in soils, the clays particle acts as a tank of corrosion inhibitor that can be release in paint films in contact with corroding agent as sodium chloride (NaCl).
For that, an anionic corrosion inhibitor was intercalated within chitosan-modified beidellite The interlayers Na+ ions of beidellite from Agadir basin (Morocco) were exchanged with chitosan biopolymer cations upon the mixture of 2 wt% dispersion of the clay mineral with an amount twice its cationic exchange capacity (CEC) of the biopolymer dissolved and protonated in heptanoic acid solution.
Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS), thermogravimetry (TG) analysis coupled to mass spectrometry (MS), carbon analysis and X-Ray Diffraction (XRD) analysis, carried out on starting beidellite and modified beidellite,.
Electrochemical Impedance Spectroscopy (EIS) measurements carried out on galvanized steel immersed in a 3 wt% NaCl solution. They revealed improvement of corrosion inhibition efficiency for coating containing chitosan-heptanoate modified beidellite in comparison with that including commercially available as Triphosphate aluminium (TPA) anti corrosion pigment.
This preliminary study mainly demonstrated on one hand the possibility to perform innovating eco-friendly inexpensive anticorrosion pigment based on animal, vegetal and mineral resources, namely chitosan, heptanoate and biedellite clay mineral respectively and, on the other hand the valorisation of these natural cheap abundant resources.

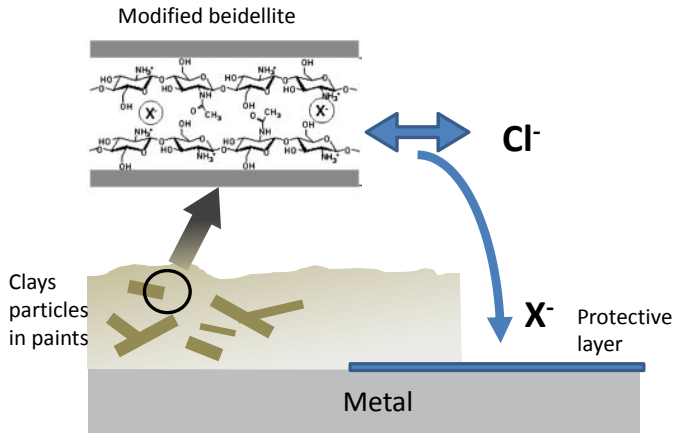

Fig. 1: Concept of corrosion inhibitor container in paints

THE BRAZILIAN COAL: CHARACTERIZATION, MORPHOLOGY AND CORROSIVENESS

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The outdoors biggest reserve of mineral coal in Brazil is located in Candiota, south of Brazil. This mineral is designated to generate thermoelectric power and heat necessary to production processes. This work aims to characterize the physical and morphological properties of the Candiota coal in addition to evaluate the corrosiveness of this mineral. The characterization was proceeding by thermogravimetric analysis, surface area analysis (BET method), electrical conductivity analysis, FTIR and Raman spectroscopies. The coal morphology was observed using scanning electron microscopy (SEM). Afterwards, the corrosion simulation was made through a direct contact with samples of carbon steel API 5L degree B with particulate matter of coal, during 6 months of exposition, being evaluated every month the attack to metallic samples. The corrosion of steel structures can occurs because of an exposition to coal particulate matter in the atmosphere or when these structures are buries a soil rich in coal. During the coal combustion S and C compounds are released to atmosphere, and these components have high affinity with oxygen and moisture, forming acidic compounds aggressive to metals surface. The process of coal extracting also generates particulate matter in the atmosphere, which can adsorb gases from polluted air. The substances formed are keeping in contact to the surface metallic exposed, promoting its degradation. The coal particles are showed in the Fig. 1. The Candiota coal is composed for aromatic groups which decomposes above 400°C and represent about 13% of the integral mass of the sample and the simple aliphatic functional groups decomposes about 280°C, being approximately 38% of the sample. The simulated metallic corrosion in direct contact with the Candiota coal sprayed (Fig. 2) indicated the nucleation of the attack after 60 days of exposure. After 90 days occurred the formation of colourful corrosion products in the vicinity of the inclusions (typical for this carbon steel type API 5L) indicating thin layers of metal oxides. And after 150 and 180 days of exposition, the corrosion products have spread for larger areas of the sample. The simulation of metallic corrosion in samples exposed to coal atmosphere indicates the formation of oxides and precipitated on the metal surface, causing a general corrosion of the samples. Even after the first 30 days of exposure, the sample of carbon steel already showed signs of corrosion on the surface, and then was possible to confirm the corrosiveness of the Candiota coal.

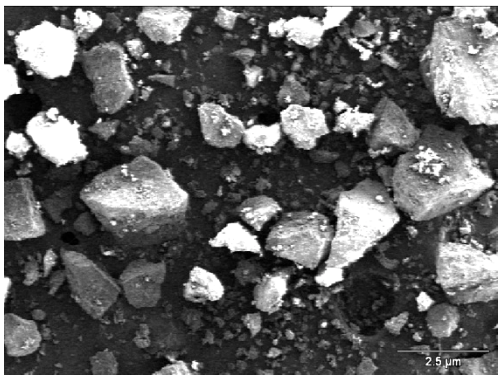

Fig. 1: Coal particles morphology.

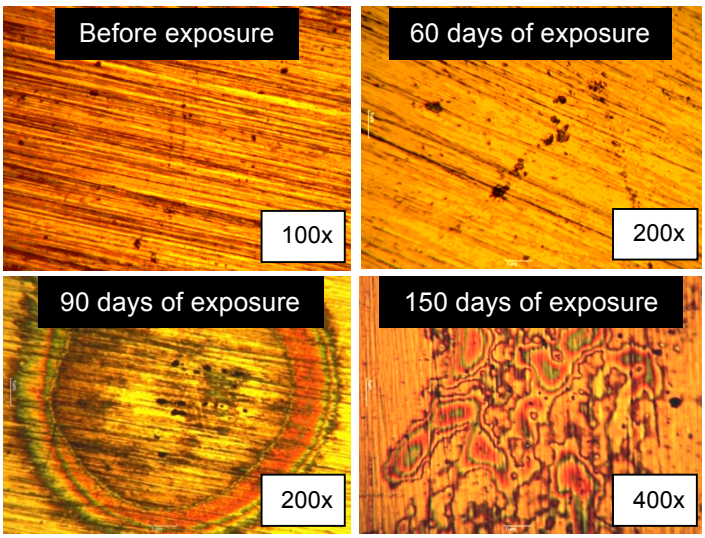

Fig. 2: Coal corrosiveness simulated in steel sample.

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A FULLY BIO-BASED POLYESTER-CO-POLYSACCHARIDE FROM MARINE RESSOURCES

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[1]*Institut de Chimie et des Matériaux de Paris Est ICMPE UMR 7182, Université Paris Est Créteil, 2 à 8, rue Henri Dunant 94320 Thiais, France.*
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Due to the global decrease of fossil fuels storage and their rising prices, a renewal of interests towards new monomers derived from renewable resources is observed. This evolution motivates research to develop novel materials labelled as environmentally-friendly,*.i.e.*, materials produced from alternative resources, biodegradable and non-toxic to the environment. Poly(3-hydroxyalkanoates) (PHAs) are a class of natural biodegradable polyesters accumulated by many bacteria, e.g. marine bacteria, as carbon and energy supply when an essential nutrient is limited. Thanks to their biocompatibility, PHAs proved to be good candidates for biomedical applications including biomedical devices, biodegradable drug carriers or tissue engineering (TE). Despite its many attributes, the intrinsic hydrophobic properties of PHAs restrict their applications as cell-colonizing materials. One approach to improve its biological properties can be made through blending PHA with hydrophilic polymers and compounds. Among polymers used in TE, polysaccharide has been widely studied due to their biodegradability, biocompatibility and capacity to mimic the extracellular matrix. Here we proposed to test a marine exopolysaccharide (EPS), HE800 which is a hyaluronane-like polysaccharide, secreted from marine bacteria originating from deep sea hydrothermal vents. Its repeating unit is a tetrasaccharide composed of two glucuronic acid units, one N-acetyl-glucosamine and one N-acetylgalactosamine. The presence of carboxylate groups on HE800 make these polysaccharides promising candidates for promoting interactions with proteins such as growth factors and cytokines. We prepared grafted and diblock copolymers.
As a preliminary study to further TE applications, we tested the ability to support cell proliferation of PHA/HE800 electrospun fibers. To achieve this goal, we first prepared HE800-g-PHA copolymer to improve the compatibility between hydrophobic PHA and hydrophilic HE800. In the grafting onto method, the carboxylic functions of PHA were activated with acyl chloride functions, allowing coupling to HE800. The chosen method for the preparation of the scaffold is a modified electrospinning system which combined both electrospinning and electrospraying. Furthermore, we showed that the electrospun PHA/HE800-g-PGA could support human mesenchymal stem cells (hMSC) adhesion and proliferation.

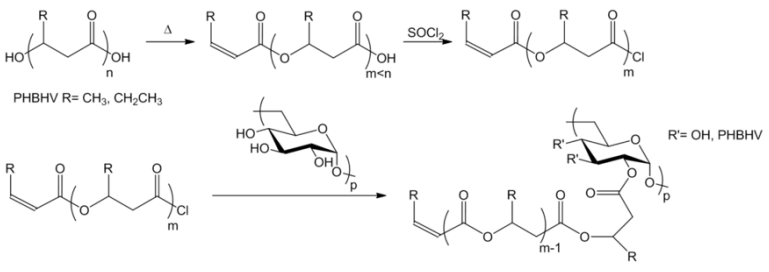

Figure 1: Reaction scheme of the preparation of HE800-*g*-PHBHV by esterification.

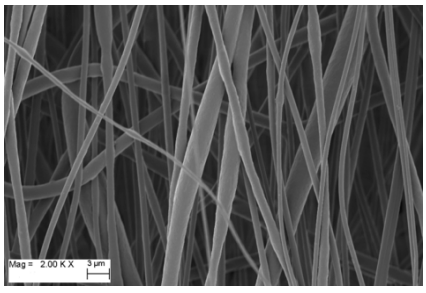

Figure 2. Nanofibers based on PHAs

P. Lemechko, E. Renard, G. Volet, C. S. Colin, J. Guezennec , V. Langlois, *React. & Funct. Polym.*, **2012**, 72, 160-167.
P. Lemechko, E. Renard, G. Volet, C. S. Colin, J. Guezennec , V. Langlois, *React. & Funct. Polym.*, **2012**, doi.org/10.1016/j.*reactfunctpolym*.2012.04.008.

CYCLOCARBONATES, BUILDING BLOCKS FOR NON ISOCYANATE POLYURETHANS

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SPECIFIC POLYMERS company is specialized in the **synthesis of monomers or polymers** bearing hetero-elements, mainly **phosphorus**, **silicon** and **fluorine** atoms. Our expertise has resulted in the R&D **production from g to kg**, of various **new breakthrough chemicals**. All around the world, we market **more than 400 references** in the most **prestigious companies and universities** (over 200 customers in 20 countries).
In the topic of Bioinspired and Biobased Chemistry & Materials, SP synthesizes many functional monomers & polymers biobased or more bioacceptable.
Non-isocyanate polyurethane (NiPUr) is a novel kind of safe polyurethane prepared by reaction between cyclocarbonates and amines [1] contrary to classical polyurethanes obtained by reaction between diamine and diisocyanate. The main problem of polyurethanes is the use of toxic components, such as isocyanates, in their fabrication process that render their production extremely toxic and dangerous.

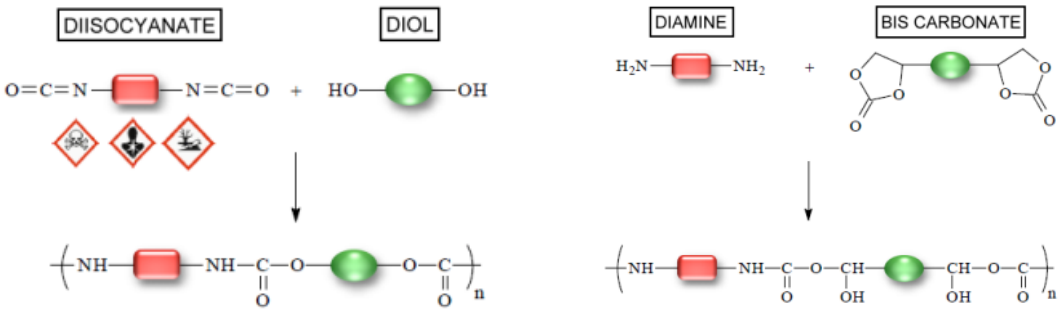
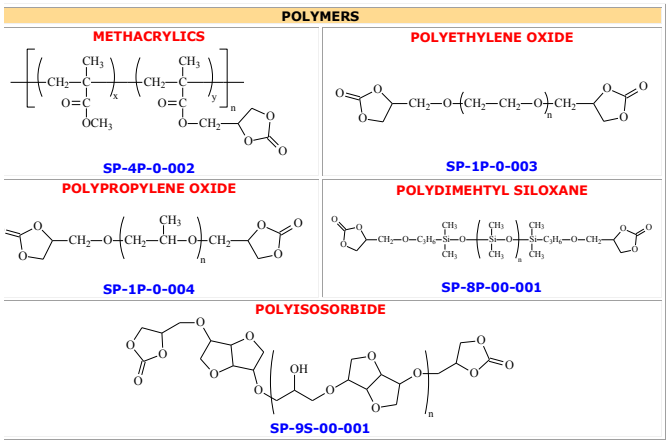


Fig. 1: Classical Polyurethanes (left) – Non Isocyanate Polyurethans (right)

Cyclocarbonates are a relatively new class of compound; they attract research interest due to their potential use in the preparation of materials not utilizing highly toxic isocyanates or their predecessors (phosgene) in their production. Cyclocarbonates can be synthesized by reacting carbon dioxide through corresponding epoxy precursors in presence of catalyst.
Due to advances in the synthesis of polymers bearing cyclocarbonates, **SP offers many NiPUr that are nowhere available** (download catalog on www.specificpolymers.fr).



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TOWARDS ARTIFICIAL PHOTOSYNTHESIS: NATURE INSPIRED PHOTOCATALYTIC SYSTEM TO REDUCTION FOR THE CARBON DIOXIDE

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The increasing demand for energy and raw materials are rising serious worries about our future. Various alternative sources of energy and fuels are under development for present and future exploitations: solar cells, fuels from biomass, wind power capacity, hydropower, photocatalytic processes (water splitting), fuels from carbon dioxide [1]. Reactions of chemical, electrochemical, biochemical and photochemical reduction of CO_2 to fuels like methane are very attractive as the convert a greenhouse gas. All over the world studies on carbon dioxide reduction have a common goal: to found the way to new materials and fuels by decreasing the CO_2 concentration in Earth's atmosphere. Many various photocatalytic systems have been studied and described in the literature but the CO_2 conversion is still low. However, the importance of artificial photosynthesis should not be overlooked. Harnessing solar energy to synthesize fuels from CO_2, reliably and inexpensively, would have a remarkably positive impact on our future.

We have studied bioinspired photosynthetic systems for CO_2 reduction to fuels [2]. Our idea combines two processes: the enzymatic reduction of CO_2 to methanol promoted by reduced form of coenzyme NADH with the *in situ* photocatalytic regeneration of NADH (Fig 1). Enzymatic reduction occurs in water and is catalysed by three enzymes: formate dehydrogenase, formaldehyde dehydrogenase, and alcohol dehydrogenase, while the necessary energy is provided by NADH which is oxidized to NAD^+. The main problem is related to the consumption of three moles of NADH per mole of methanol produced. In Nature, NAD^+ is reduced back to NADH with help of solar light; in the industrial application such reduction would have to be performed implementing the most energetically and economically convenient technologies, like photocatalysis. In our studies photocatalysts based on semiconductors were tested for the reduction of oxidized form of the coenzyme to NADH.

Studies on NADH regeneration in aqueous solution were the first step in research project on carbon dioxide reduction to methanol using photocatalytic-enzymatic hybrid systems. Our goal was to reach a relatively high efficiency of reduction NAD^+ under visible light irradiation and high selectivity to isomer 1,4-NADH. Several semiconducting photocatalysts active in visible light have been prepared and characterised: transition metal oxides and composites of oxides, metal oxides modified with organic and inorganic compounds and metal-doped sulphides. Several methods and analytical techniques have been used for understanding the mechanism of this photocatalytic process, such as NMR, UV-Vis absorbance spectroscopy, fluorescence spectroscopy, HPLC.

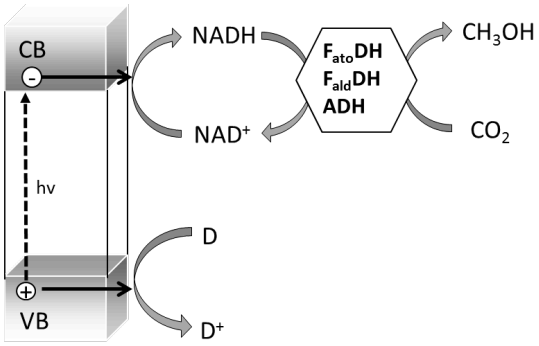

Figure 1. Hybrid photocatalytic-enzymatic system for CO_2 reduction.

Combination of the enzymatic method of carbon dioxide reduction with photocatalytic regeneration of NADH is a modern, bioinspired, novel and promising approach to convert carbon dioxide into methanol. The tested system is interesting because NADH is produced in a clear, cheap process without the use of electricity nor thermal energy.

TB acknowledge the financial support from Foundation for Polish Science for the research grant within the VENTURES initiative cofinanced by the EU European Regional Development Fund.

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INTERACTION OF METRIBUZIN WITH ZINC ORGANOMETALLIC COMPOUNDS

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Particular chemicals like pesticides which use, in agriculture, became inescapable are engendering an environmental pollution and more particularly that of soils.
It is urgent, for preservation of public health, to reduce at most our exposure to these substances and to operate everything to reduce and control these pollutants. Some conventional adsorbing product such carbon F400 are frequently used.

The adsorption on the synthetized metal organic complexes may be a alternate technique to disinfect soils and waters polluted by pesticides and other chemicals.
In this context, some coordination compouds of Zinc were tested in the adsorption of mitrobuzin present in contaminated water. The retained organic molecules are natural products (flavonoids and purines)

The preliminary results seems encouraging and we report them here.

ONE-POT SYNTHESIS OF EPOXY-CHALCONE CATALYSED BY POLY-L-LEUCINE IMMOBILIZED ON HYDROTALCITE

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A major research in the field of synthesis of products for fine chemistry and pharmaceuticals is done in the study of asymmetric catalysis reactions. The major difference between synthetic asymmetric catalysts and enzymes is that the synthetic asymmetric catalysts activate only one substrate in an intermolecular reaction, whereas the enzymes can activate both substrates and can also control their orientations. For example, the class II metal-dependent aldolasa can activate the ketone enolate and at the same time the aldehyde. [1] The dual activation is fundamental to promote with total stereoselectivity the reaction from stable substrates under mild conditions. This type of synergistic cooperation can be developed using artificial asymmetric catalysts base on the concept of multifunctional catalysis. Therefore, efforts to obtain new catalysts inspired from Nature are a very interesting challenge.

The aim of this study is to develop a protocol for obtaining epoxy-like compounds with high conversion and enantioselectivity using a one-pot Claisen-Schmidth-Julia Colonna reaction (figure 1).

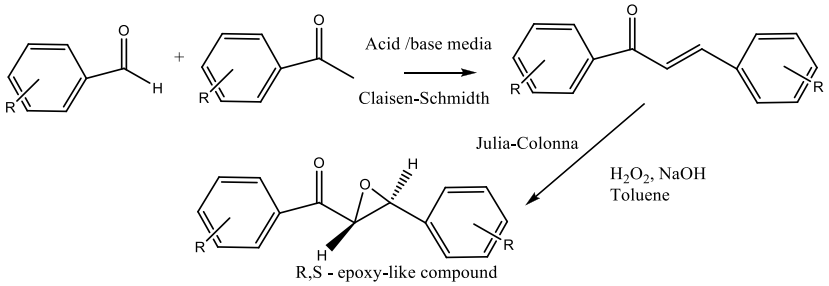

Fig.1 One-pot reaction of Claisen-Schimdt – Julia-Colonna

There are few examples in literature of heterogeneous systems able to carry out this type of one-pot reaction. Choudary et al. used a nanomagnesium oxide (NAP-MgO) for this type of tandem reaction, but the conversion and enantioselectivity obtained were moderate. [2] Wang et al. used a novel oxidation system formed from trichloroisocyanuric acid with an inorganic base such as potassium hydroxide, being able to obtain epoxides with high conversion and enantioselectivity. Unfortunately, the recovery and reuse of the catalyst was not studied. [3] Taking into consideration the properties of poly-L-leucine, Wang have used the polymer modified with imidazole as a reaction catalyst for the same tandem reaction. After 72 h of reaction high enantioselectivity was obtained with good conversions [4].

The catalytic system proposed for this one-pot reaction consists of poly-L-leucine immobilised on a hydrotalcite material. The hydrotalcite contains a Al:Mg ratio of 2:1 and was calcinated and rehydrated before immobilization, to increase the number of the basic sites and to favour the intercalation of the polymer. The poly-L-leucine was obtained through ring opening polymerisation of NCA-L-leucine. The immobilization was carried out in the presence of water. The catalytic performance of different nanohybrid materials leads to high activity and enantioselectivity with unique advantages: they do not require a pre-activation time and can be easily reused at least for four consecutive runs. Besides the effect of catalyst it was also studied the effect of temperature on the reaction performance. The products were characterized by NMR, HPLC spectroscopy and the polymer through Maldi-Tof, TGA and XRD analysis to obtain a complete view of the process and also to determine the activity of the catalyst.

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INTERACTION OF SUBSURFACE PESTICIDES WITH SOME METAL-ORGANIC FRAMEWORKS

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Particular chemicals like pesticides which use, in agriculture, became inescapable are engendering an environmental pollution and more particularly that of the waters as well of surfaces as ground-water sheets.
It is urgent, for preservation of public health, to reduce at most our exposure to these substances and to operate everything to reduce and control these pollutants.
So, the presence of pesticides in drinkable waters is severely regulated and the producing companies of water, to conform to the established standards, are obliged to include in their networks of water treatment, processes to eliminate them.

The adsorption on the synthetized metal organic complexes may be a technique to disinfect waters polluted by pesticides and other chemicals.
In this context, some coordination compouds of manganese, copper, zinc and cobalt were tested in the adsorption of mitrobuzin present in contaminated water. The retained organic molecules are natural products (flavonoids and purines)

The preliminary results seems encouraging and we report them here. They are compared to those obtained with a classic adsorbing agent, namely powdered activated carbon F400.

DNAZYME WITH PEROXIDASE ACTIVITY CATALYZES SILVER DEPOSITION

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DNAzymes with peroxidase-mimicking activity found wide application in biosensing field. Due to their advantages in comparison with protein enzymes (thermal stability, simple synthesis and purification) they can successfully replace horseradish peroxidase (HRP) in bioanalytical applications [1]. Peroxidase-mimicking DNAzyme should adopt a G-quadruplex topology and form a complex with hemin in order to exhibit catalytic activity. Such a system can successfully catalyze redox reaction between hydrogen peroxide and a suitable substrate, for example, luminol (chemiluminescence) or ABTS (colorimetry) [2]. Development of new peroxidase substrates is a very active area of research, which involves attempts to use other, more sensitive measurement techniques. Our interest is focused on the amplification reaction of catalytic silver deposition. This reaction is well known and widely used in systems that exploit HRP. We have investigated the possibility of adapting silver deposition reaction to systems containing peroxidase-mimicking DNAzymes and prospect of its practical employment in combination with SPR or LSPR techniques.

Despite the fact, that the reaction of silver deposition catalyzed by HRP is well known, the mechanism and reaction details are not fully understood. Our preliminary studies involved spectrophotometric homogeneous tests of Ag^+ reduction with a commercial Silver Enhancing Kit in the presence of DNAzyme. As a G-quadruplex platform to construct DNAzyme with hemin, we used a PS2.M oligonucleotide (3'GGGTAGGGCGGGTTGGG5'), which possesses high peroxidase activity. The absorption band at 406 nm was chosen to monitor formation of Ag nanoparticles that accompanied catalytic silver reduction. Significant increase in absorbance confirmed that DNAzyme with peroxidase activity catalyzed the reaction of silver deposition.

The silver deposition reaction enhanced by DNAzyme was further studied using SPR and LSPR (Localized Surface Plasmon resonance) techniques. The Au surface was modified with a PS2.M oligonucleotide bearing a $TTTT(CH_2)_6SH$ linker. Preliminary experiments confirmed binding between hemin and G-quadruplex forming structure. We also observed significant changes in light scattering of gold nanoparticles after silver deposition. Silver deposition catalyzed by DNAzyme was much more effective comparing with the reference reaction without hemin. These promising results give future prospects for developing simple and effective bioassays by combining the DNAzyme-catalyzed silver deposition and LSPR technique.

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DESIGNING AN ORGANIC-INORGANIC HYBRID CATALYST BASED ON CARBON NANOTUBES AND POLYOXOMETALATE FOR BIOMIMETIC ALKENE EPOXIDATION

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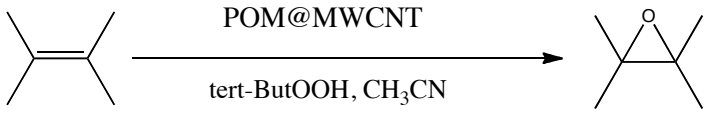
In recent years, polyoxometalates (POMs) have received considerable attention because of their great ability in analytical chemistry, catalysis, medicine, and material science [1]. Interestingly, catalysis and material science are still the two main fields of applications of POMs [2,3]. Among the polyoxometalates, most of researches in catalysis utility have been assigned to Keggin and Wells-Dawson structures [4]. Additionally, synthesis of multifunctional hybrid materials by using covalently linked polyoxometalates and organic molecules have drawn tremendous attention in the last decades [5].

Therefore, for meeting our aim to broaden the scope of catalytic activity of these compounds, we centralized our consideration on working with Organic-Inorganic polyoxometalate hybrid materials and using them as a catalyst in organic reactions. Regarding the organic reactions, designing biomimetic systems, which mimic the function of P-450 enzymes, is an important subject in catalysis field and also from biological aspects [6]. In this respect, first we design a nano-sized heterogeneous catalyst, which are composed of polyoxometalate that covalently linked to the functionalized multi-wall nanotubes (MWCNT). In the second step, we utilize this heterogeneous hybrid catalyst in alkene epoxidation using t-butyl hydrogen proxide (scheme 1).

Since we use the both polyoxometalate structure and carbon nanotube in catalyst structure, our catalyst shows the properties of these two compounds and therefore, we observe the outstanding results in epoxidation process. Interestingly, the present methodology offers several advantages such as short reaction times, high yields, simple procedure, non-toxicity and low cost, furthermore, this new heterogeneous catalyst demonstrates high reusability in the oxidation reactions, in which the catalyst were reused several times without significant loss of their catalytic activity.



Scheme 1: shematic representation of alken epoxidation by nanosized catalyst

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HIGH SELECTIVE OXIDATION BY HYDROGEN PEROXIDE IN THE CONDITIONS OF ITS COHERENT SYNCHRONIZATION WITH H_2O_2 DECOMPOSITION

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At the present work it is shown how interaction between reactions may be qualitatively and quantitatively assessed and kinetic analysis of complex reactions with under-researched mechanisms may be performed with simultaneous consideration of the stationary concentration method. Using particular example, for instance, ethylene oxidation into acetaldehyde, demonstrate experimental approaches to the study of interfering reaction dynamics and, with the help of the determinant equation, the potential abilities of reaction media are assessed and the type of chemical interference determined.

The gas-phase monoxidation of ethylene by hydrogen peroxide on the heterogeneous catalyst (per-FTPhPFe^{3+}OH/Al_2O_3) was shown that biomimetic oxidation of this substrate by hydrogen peroxide to be coherently synchronized with the decomposition of H_2O_2 [2].

The coherence condition is expressed by following equation:

$$\frac{1}{\nu} f_A = f_{Ind} = f_{A_1} + f_{A_2} = f'_{A_1} + f'_{A_2} = f''_{A_1} + f''_{A_2} = ... = const \quad (1),$$

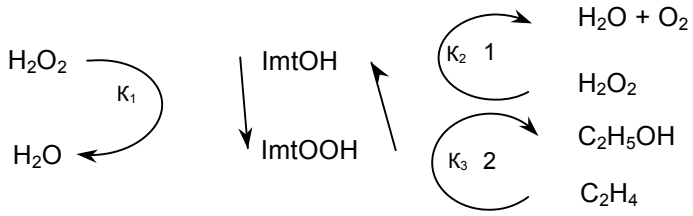
where f_A - is the amount of actor (hydrogen peroxide), f_{A_1} and f_{A_2} - are the amounts of the actor consumed in the primary and secondary reactions, respectively.

The quantitatively determination of the inductive action of H_2O_2 on substrate oxidation was realized by determinant equation (2):

$$D = \nu(f_{A_1} / f_{Acc} + f_{A_2} / f_{Acc})^{-1} \quad (2)$$

The value of determinant D = 0.1÷0.4 on the chemical interference scale falls within the range for conjugated reactions (0÷1).

In the chemical system studied biosimulator catalyzes two interrelated (catalase and monooxygenase) reactions, which are synchronized and proceed according to the following mechanism:



where ImtOH is per-FTPhPFe^{3+}OH/Al_2O_3 biosimulator, ImtOOH is per-FTPhPFe^{3+}OOH/Al_2O_3 intermediate, (1) primary catalase reaction and (2) secondary monooxygenase reaction.

With determinant equation (2) the kinetic equation for ethylene consumption rate is derived:

$$r_{Acc(C_2H_4)} = k_2 \frac{k_1}{k_3} \frac{D[H_2O_2]^2[\mathrm{Im}tOH]}{[C_2H_4]} \quad (3)$$

Using experimentally obtained values of $r_{C_2H_4}$ and D, the appropriate kinetic calculations were carried out. Therefore, equation (3) adequately describes the kinetics of interfering reactions.

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INVESTIGATING THE THERMORHEOLOGICAL PROPERTIES OF CONVENTIONNAL AND BIOBASED ALKYD RESINS.

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Alkyd resins have been introduced in the 1930s and contribute to about 70% to the conventional binders used in surface coating today.[1,2] The ever-increasing environmental consciousness is pressuring for the transition from petrobased products to biobased products with equivalent performances. Up to recently, solvents such as white spirit or toluene were widely used to reduce and adjust the paint viscosity. These solvents were the major source of petrobased carbons in alkyd paints. In recent years, critical developments in the surfactants world enable the design of waterborne alkyd emulsions and high solids alkyds as more environmentally friendly binders for coatings.
Alkyd resins are products of polycondensation reaction between polybasic acid and polyol modified with fatty acid and monoacid.[3,4] Therefore, alkyd resins have, by definition, high content in renewable raw materials such as fatty acid and polyol. After the solvent-to-water transition, the last unresolved challenge for alkyds producers remain the replacement of petrobased raw materials such as phthalate and benzoic derivatives. Some attempts were made to use dimerized fatty acid as a dibasic acid substitute of the phthalic anhydride but no information on key polymeric properties such as the glass transition temperature were reported for these alkyd resins.[5,6]
Rheological properties are critical in paint applications and are closely linked to the monomers used during polymerization. Switching from phthalic anhydride to other bio-sourced acids could have high impact on these rheological properties. Therefore, bio-sourced acids have to be carefully selected depending on their effect on the final rheological properties of the alkyd resin. Alkyd viscosity values are obtained from falling-ball viscosity test at 110°C. Since viscosity is a macroscopic expression of molecular mobility, we linked these viscosity values with actual glass transition temperature of resin determined by DSC. Based on this correlation, we set up a calculation method for predicting glass transition temperature of alkyd resins based on their compositions, using Fox equation for copolymer as a basis.[7] Arbitrary pseudo-glass transition temperature values were affected to lateral groups depending on their plasticizing or anti-plasticizing effects. While improvements in our calculation methods are in progress and additional bio-sourced raw materials are under evaluations, some preliminary results will be presented here.

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FLUORINATED MULTI-FUNCTIONAL COATINGS: COMBINING SURFACE CHEMISTRY AND PERFORMANCES

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Fluorinated compounds are among the most versatile products of the chemical industry, appearing in several industrial application such as coating, textile, leather, pharmaceutical, detergency, petroleum recovery, electronic printing, magnetic [1]. During the past fifty years commercial interest in fluorinated compounds has burgeoned beyond all expectations in business opportunities.
Maflon scientific research laboratory is based on the chemical study of fluorotelomers, obtained by a controlled polymerization of tetrafluoroethylene [2]. Maflon Laboratory uses these molecules to prepare fluorinated materials such as alcohols, glycols, olefins, (meth)acrylics, epoxydes [3], silanes [with a base structure $F(CF_2)_n (CH_2)_mX$ where X is the reactive group.
Fluoropolymers as poly(meth)acrylates, polyurethane, polysiloxane for surface treatment to improve oleo and hydro repellency, fluorosurfactants [4,5] used as wetting, leveling agents for floor polish, wax formulation [6], paint and coating.
Maflon products include the Lineplus line, based on C_8 technology, and the new brand Hexafor based on C_6 technologies. Maflon research is constantly involved with the development of new fluorinated materials to lead innovative and customized solutions for different applications. Maflon products can be applied without altering the aspect and the touch sensation of the original substrate.
The quality assurance and control procedures [7], including equipment operations and maintenance, and all procedures as well analytical methods [8] as raw materials and finished products control, are made in according to international standard (AATCC, ASTM, DIN) or to customers' required standard.
The list of commercial products includes nonionic and anionic fluorosurfactants, perfluoroalkanes, semifluorinated alkanes, fluorinated polyacrylates-methacrylates, fluorinated siloxanes, fluorinated silicones [9-10], fluorinated polyurethanes, fluorinated intermediates.

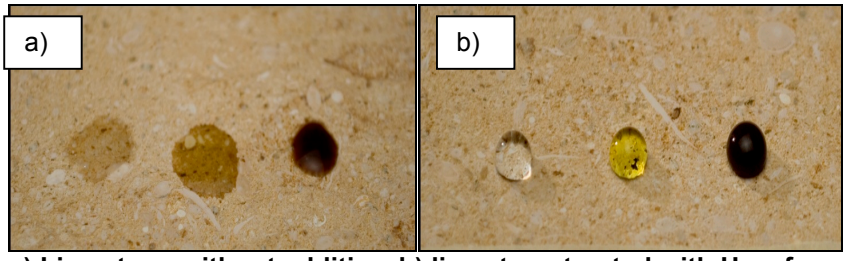

Fig. 1: a) Limestone without additive, b) limestone treated with Hexafor additive

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ELABORATION OF SUPERHYDROPHOBIC SURFACES WITH CONTROLLED MORPHOLOGY FOR ANTIBACTERIAL ADHESION

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The bacterial adhesion and the formation of biofilm are natural and spontaneous processes. This phenomenon happens whatever the nature of bacterium, surrounding fluid and receiving substrate (plastics, metals, glasses, ...).

Bacterial adhesion depends on physical chemistry interactions between the bacteria and the receiving substrate. Tamada and Ikada showed that the nature of material and its characteristics of surface, such as superhydrophobic or hydrophilic character, can affect the development of a biofilm to obtain « anti-adhesive » surfaces. [1] Superhydrophobic surfaces prevent the wetting which may promote the "sliding" of the aqueous medium on the surface. Hence, the interactions with bacteria may also be reduced.

The superhydrophobicity is associated with the chemical functionality of the coating and its roughness. These « anti-adhesive » surfaces can be made by surface structuring and coating with an intrinsically hydrophobic polymer. Electropolymerisation is a simple, inexpensive and perfectly manageable method allowing to structure and to functionalize surfaces in order to make them superhydrophobic. [2]

The major challenge is the control of roughness: actually, roughness induces the superhydrophobic properties but a suitable morphology is required to limit mechanical trapping of bacteria. In this study, we present superhydrophobic polymers with different surface properties and compare their impact on bacterial adhesion.

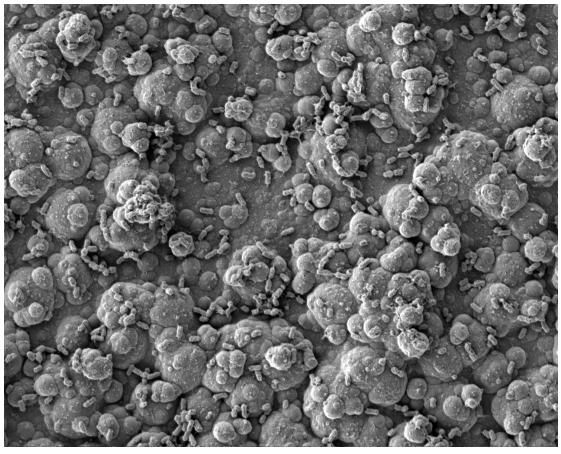

Fig. 3: Trapped bacteria on rough superhydrophobic surface

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CONCEPTION AND ELABORATION OF VERSATILE BIO-INSPIRED SURFACES

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Superhydrophobicity results from the combination of low surface energy materials with the surface structuration at micro and/or nanometer scale. Such surfaces are interesting because of their expected self-cleaning or anti-contamination property that could be useful in various fields such as in biomedical devices or aeronautics for example.
Electropolymerization is a quick (deposition and structuration in one-step) and reproducible method to obtain superhydrophobic surfaces. Moreover, electropolymerization of conducting polymers is a versatile technique. Indeed, not only the monomer chemical structure (polymerizable core, substituent) [1-2] but also the electrochemical parameters such as doping agent, deposition charge or solvent allow to control the surface growth and their morphology in order to obtain surfaces with various water-repellent properties and even reach superhydrophobic properties.
In most publications on such surfaces, the general approach is the use of highly fluorinated tails (during the process or with a post-treatment) to reach water-repellency properties. However, as observed in nature, fluorine is not necessary and can present consequent environmental impacts.
This work presents the electropolymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) derivatives containing an alkyl chain group in 2-position and the characterization of the obtained films to reach bio-inspired versatile wetting surfaces [3].

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SILICA NANOPARTICLES DISPERSION INTO FLUOROCARBON OR HYDROCARBON POLYMERS: STUDY IN FLUID MATRICES AND ON A SUPPORT

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Due to the increasing interest on silica nanocomposites in a lot of fields like drug carriers, nanocomposite materials, a lot of approaches that aim at the functionalization or the grafting of silica nanoparticles in order to attune them with the matrices (solvent or polymer ones) are published in the literature [1-3]. The main difficulty encountered is the stability of the nanoparticles dispersion in the surrounding substance. For a better control of this parameter in fluid matrices, we wanted to explore a new concept: the grafting of silica nanoparticles on amphiphilic and thickening ASE and HASE polymers.

ASE (alkali-swellable emulsion) or HASE (hydrophobically alkali-swellable emulsion) polymers have been extensively studied due to their ability to form three-dimensional networked gels and were employed in lot of domains like cosmetics, paints and anti-icing fluids. The backbone of these copolymers is constituted of acrylic acid (AA), monomers with short hydrophobic chain and small amounts of hydrophobic pendant groups (macromonomers). These thickening agents typically combine two properties: the solubility in basic water (pH>7) due to the presence of carboxylic groups that ionise and provoke the increase of hydrodynamic volume, and the existence of Van der Walls interactions between the polymeric chains for an increase of the aqueous solution viscosity [4].

This work presents the synthesis of new hydrocarbon-fluorocarbon thickening agents and their covalent grafting with silica nanoparticles *(fig. 1)*. A dynamic light scattering study of their resulting dispersion in acid and basic aqueous medium will also be detailed to optimise the dispersion efficiency of the nanoparticles. Then, coatings realised with these dispersions on glass slides were done to visualise the dispersion of nanoparticles on supports. Atomic Force Microscopy (AFM) put in evidence the influence of hydrocarbon or hydrocarbon-fluorocarbon polymers on silica nanoparticles distribution on a support.

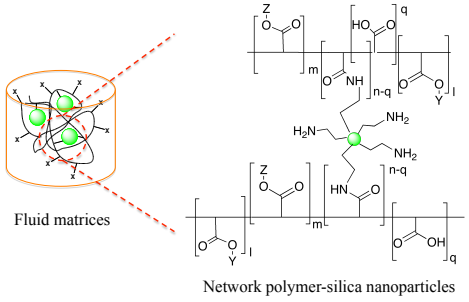

Fig. 1. Scheme of network polymer-silica nanoparticles in fluid matrices. X = monomers of polymeric chains. Y = short hydrocarbon or fluorocarbon chain and Z = hydrocarbon or fluorocarbon macromonomers.

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STUDIES OF PROPERTIES OF NANOCOMPOSITES BASED ON CLAYS AND SEMI-FLUORINATED SURFACTANTS (SURFMERS)

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Mineral clays are one of the most studied inorganic fillers for polymer based nanocomposite materials (figure 1). In fact their availability is quite wide and they can improve the matrix performances assuring better mechanical and thermal properties, higher scratch resistance, barrier and anticorrosive properties. The most studied clay for the preparation of nanocomposites is montmorillonite. In its natural state it contains small cations, normally Na^+ or K^+, in between its layers (interlayer space or gallery space), and small cations can be exchanged for another cation in aqueous solution.

Surfactants containing fluorine atoms have been proven to be an interesting class of materials with remarkable properties, including low surface energies, low dielectric constants and refractive indices, high chemical and thermal stabilities and solubility in supercritical surface energies CO_2.

In the present work we have synthesized some fluorinated surfactant monomers (surfmers) whose structure is made of a fluorinated tail, an ammonium salt head group and an acrylic polymerizable moiety as represented figure 2. We will discuss on the properties of these surfactants and their incorporation in montmorillonite clay.

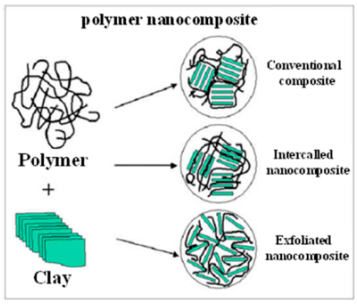

Fig. 1: exfoliation of clay using surfactant polymers

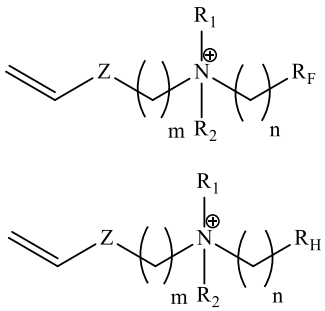

Fig. 2: schematic structures of the investigated polymerizable surfactants (surfmers)

SELF-REPLENISHING SUPERHYDROPHOBIC SURFACES

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Self-healing materials are currently one of the most active research topics in materials science. While many strategies and mechanisms have been reported to repair mechanical (bulk) properties, [1,2] the recovery of surface properties or surface-related functionalities has been scarcely addressed so far.

In our group we reported a self-healing principle which allows the material to self-replenish the surface with new chemical groups, [3] upon a surface damaging event (*e.g.* scratches). It was shown that low-surface-energy poly(urethane)-based materials can replenish *spontaneously and instantaneously*, the new surfaces created after intentional damage, with a certain concentration of the low-surface energy groups (*e.g.* fluorinated dangling chains). This self-replenishing mechanism is driven by differences of energy of the new surfaces and occurs through the surface-reorientation of the low-surface-energy groups, which are homogeneously distributed and covalently bonded to the cross-linked network.

While this self-replenishing mechanism proved to be very efficient on smooth polymeric surfaces we are currently investigating how to apply this principle on structured-surfaces, to recover not only the surface chemistry but also the surface-related functionality.
In Nature, we can find many examples of structured surfaces (Fig. 1a) which endow peculiar properties to the living organisms, *e.g.* special wettability, improved adhesion and tuned optical properties (color or reflectivity). Accordingly, many synthetic surfaces which combine the proper surface chemistry and topology have been developed to reach advanced properties, *e.g.* self-cleaning (*Lotus effect)*, improved adhesion (*Gecko effect*) or tunable-structural colors ("*butterfly wings effect*").
These biological surfaces recover from surface damage through complex self-healing mechanisms triggered by external-stimuli which induce the transport of new material to the damage *loci*. Keeping these principles in mind we applied the self-replenishing principle described above to obtain robust and easy processing superhydrophobic coatings (Fig. 1b) which are able to self-repair their surface chemistry.

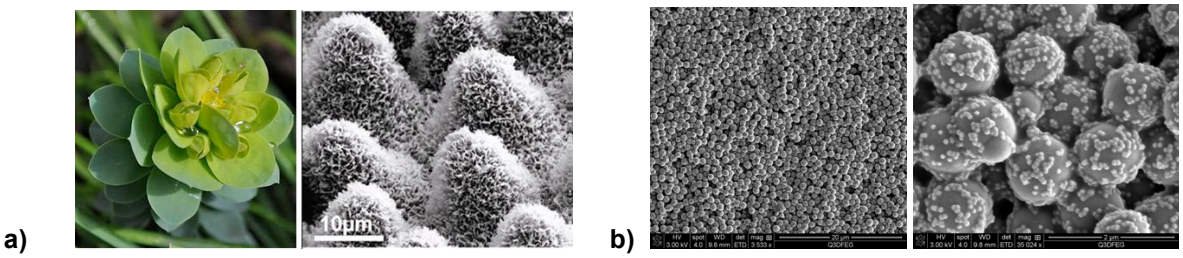

Fig. 1: *a*) euphorbia mysinites leaves and respective surface-microstructure (SEM image) and *b*) superhydrophobic self-healing coating (SEM images).

In this work we will discuss the preparation of these coatings from an *all-in-one* initial mixture of the components through a simple chemical method and a one-step procedure.[4] By incorporating inorganic nanoparticles in the polymer system, we were able to design surface-structured coatings (Fig. 1b) which are able to replenish the new surfaces created after damage with low-surface energy groups, partially responsible for functionality of the material, *i.e.* superhydrophobicity. By these means the functionality of the coating is recovered and its performance (self-cleaning behavior) is kept at a high level for a service life-time.

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SUPERHYDROPHOBIC COATINGS BASED ON SILICON OXIDE NANOPARTICLES

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Superhydrophobic materials are desirable for many industrial and biological applications such as antibiofouling paints for boats, antisticking of snow for antennas, self-cleaning windshields for automobiles [1]. The increase of wetting contact angles to 150º and above reached at the expense of a microrelief with a controllable roughness of a surface layer in a combination to water-repellent materials so-called «lotus effect». [1, 2] Plasma or laser etching, an engraving, lithography and controllable aggregation of nanoparticles on the surface from colloid solution are known for creation biomimetic superhydrophobic surfaces. [1 – 3]

In this work the layers of silicon oxide particles (diameter ~ 10 nm, Aldrich) were formed on glass substrate of rectangle shape with area ~ 4 cm^2 by drop-coating method [2] from polyvinyl alcohol (PVA) colloid solutions of SiO_2. Their treatments with octadecylthrichlorosilane (OTS) solution in hexane give rise to formation of biomimetic superhydrophobic coatings. Linear microtribometer was used for the testing of samples stability. [4] Conditions of the testing were the next: normal load is 0.3 N, indenter – 3 mm diameter steel ball, stroke – 3 mm, linear speed is 4 mm/s.

Deposition of SiO_2 nanoparticles from the PVA colloid solution on a glass plate result in their aggregation on the surface (Fig. 1) and the formation of the layer with high surface roughness (R_a ~ 2.8 μm, R_{max} ~ 18 μm). Therefore, the subsequent modification of the SiO_2 film by OTS provides a superhydrophobic surface with a wetting contact angle ~ 157º (Fig. 1, b). Such coatings are stable against mechanical influence of the indenter up to 640 sliding cycles, which are two orders of magnitude higher than that for SiO_2 layer.

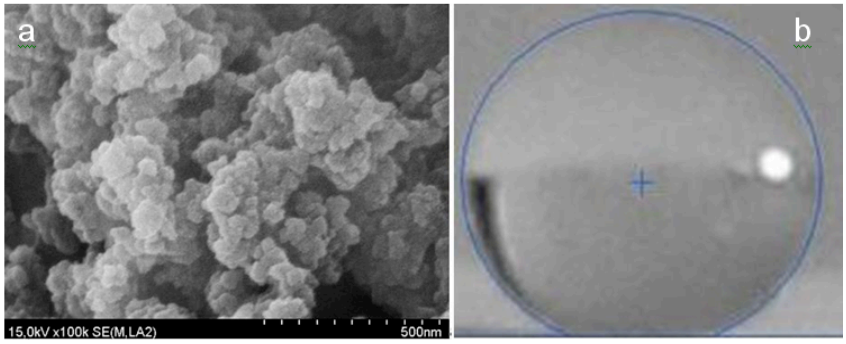

Fig. 1: (a) SEM image of the coating of silica nanoparticles in PVA formed on glass by drop-coating method and modified by OTS, (b) water drop on its surface

It is shown that layers formed on glass by drop-coating method from polyvinyl alcohol colloid solutions of silica nanoparticles modified by octadecyltrichlorosilane are found to acquire superhydrophobic properties and can be used to create self-cleaning surfaces.

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APPLICATION OF BIOINSPIRED TOPOGRAPHIC GRADIENTS IN MARINE ANTIFOULING RESEARCH

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For the development of environmentally friendly antifouling coatings it is important to understand the interaction between marine organisms and surfaces in greater detail. [1, 2] Among the different surface cues, the settlement of cells and larvae has been found to be influenced by surface microtopography. [3] In this study, the influence of surface topographic gradients on the settlement of zoospores of the green alga *Ulva* was investigated. Honeycomb structures, which can frequently be observed in nature, such as the skin of the pilot whale, [4] the shell of the turtle and the eyes of crab, etc. has been considered to facilitate the antifouling function of natural surfaces. A gradient of honeycomb microstructures with continuously changing size were prepared by hot embossing, [5] and the effect on the density of spores that attached in laboratory assays was quantified. The highest density of spores was found when the size of the microstructures was similar to, or larger than the size of a spore. With decreasing size of the honeycombs, spore settlement decreased. Interestingly, spore settlement correlated with the Wenzel roughness of the surfaces. During settlement, “kink positions” on the surface played an important role and resembled preferred attachment positions. The gradients furthermore allowed determining the minimum pit size chosen by the spores to squeeze in and settle.

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COLORED AND TRANSPARENT SUPERHYDROPHOBIC SURFACES

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Natural surfaces, such as lotus leaves, gecko feet hairs and water strider legs are known for their extremely high water contact angles (> 150^{o}) and very little flow resistance. These superhydrophobic surfaces are of interest for numerous applications, including anti-fouling coatings, impermeable textiles, microfluidics, lab-on-a-chip devices and biotechnology. Recently, *Morpho* butterfly wings, which are known for their brilliant blue color as a result of quasi-multilayer interference, are also found superhydrophobic due to the nano-roughness appeared on top of the multilayers. Meanwhile, there have been increasing interest in energy efficient coatings that are both self-cleaning and transparent for potential applications, such as solar cells, window treatment, and optical equipment. By inducing microphase separation of the polymer chain segments using a nonsolvent during the rinsing step in holographic lithography process, we introduced nano-roughness on the 3D photonic crystals, which exhibited both structural color and superhydrophobicity (Fig. 1a) [1]. Further, we demonstrated transparent superhydrophobic surface by spin coated hydrophobic silica nanoparticles on a wide range of substrates (e.g., Si, glass and plastics) [2]. The nanoparticles were found to form a nearly close-packed assembly, thus, effectively minimizing the exposure of the underlying substrate while offering sufficiently trapped air pockets. The nanoparticle surface was also highly transparent, > 95% transmission in the visible wavelength. The combination of self-cleaning and photon management offers new opportunities to realize multi-functional materials for solar applications.

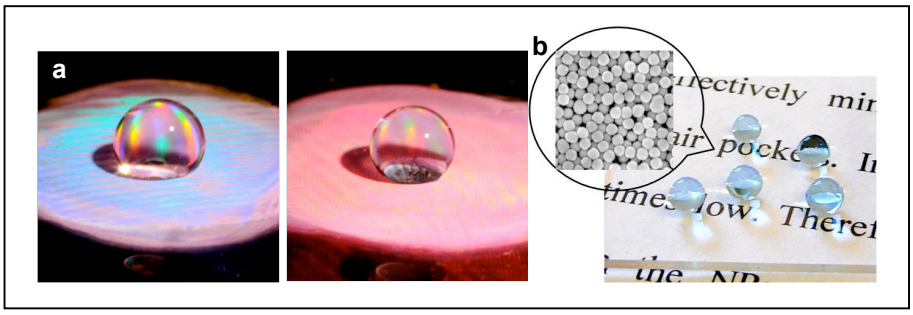

Fig. 1: Optical images of a) 3D photonic structures with different degrees of hydrophobicity and b) nanoparticle assembly that offers transparent superhydrophobicity.

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SURFACE PROPERTIES OF SPIDER SILK PARTICLES: COMBINING DIRECT FORCE MEASUREMENTS AND ELECTROPHORETIC TECHNIQUES

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Spider silk protein fibers have outstanding mechanical and biomedical properties. Recombinant spider silk proteins on the basis of the major ampullate spidroins of the dragline silk of the European garden spider *Araneus diadematus* can assemble into a huge variety of different morphologies such as films, hydrogels and particles. In addition, good biocompatibility and weak immune response have been reported for these proteins. Thus, spider silk materials are interesting for medical applications like wound dressings, implant coatings, and drug delivery.[1]
Surface properties (e.g. charge, chemistry and adhesion properties) are crucial parameters for these applications. The properties of spider silk proteins on the molecular level have been studied intensively in the past years. However, the properties of particles formed from spider silk proteins have been examined to a smaller degree.
Here, we report the characterization of the surface charge properties of recombinant spider silk particles by the combination of two techniques from colloidal science.[2] The particles have been prepared by salting-out the protein.[3] The colloidal probe technique based on the atomic force microscopy (AFM) was used to probe long-range interaction forces between the spider silk protein particles and another colloidal particle. The setup is schematically shown in figure 1. The surface potentials were obtained in the framework of the Poisson-Boltzmann theory. In addition, steric interaction forces were determined as an additional force contribution indicating a diffuse particle surface. These direct force measurements have been compared to the electrophoretic mobility of the same spider silk particles. Our results are of importance to understand the stability of silk particle suspensions and their adsorption to solid interfaces.

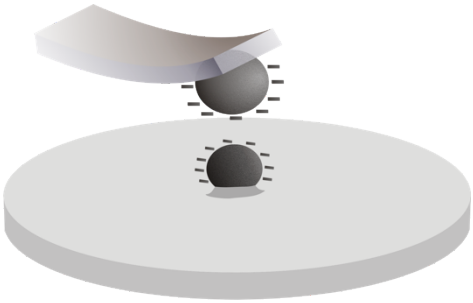

Fig. 1: Setup for direct force measurements in sphere-sphere geometry

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FUNCTIONALIZED SILICA AEROGEL–POLY(METHYL METHACRYLATE) COMPOSITES FOR POTENTIAL USE IN BONE CEMENTS

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A significant portion of 2bone cements that are currently in use are either copolymers or organic/inorganic composites of poly(methyl methacrylate) or its hydrophilic derivatives. Increasing their mechanical strength and hardness, as well as wear resistance, and tissue compatibility are still major goals of bone cement research today. Pmma combined with inorganic fillers, and nano-fillers exhibit significantly improved mechanical properties.

Aerogels are the lightest solids on Earth and show quite unique physical properties like extremely high specific surface area, relatively high mechanical strength and good biocompatibility. Some aerogels are already in use in the pharmaceutical industry as fillers, others are under testing for use as controlled-release drug carriers.

Here now we present the synthesis of functionalized silica aerogels, their first incorporation into poly(methyl poly(methyl methacrylate) (pmma) matrix, as well as mechanical testing and in vitro study of biocompatibility of the composites. Aerogels were prepared from tetramethoxysilane and the corresponding monofunctionalized trimethoxysilanes in water-methanol mixtures by base catalyzed sol-gel process, then aged, solvent-exchanged and dried under supercritical conditions with carbon dioxide. Natural silica aerogels as well as phenyl and C16-functionalized aerogels were used as received. Some neutral aerogel was also heat treated at 500 °C before embedding in pmma. Pmma-aerogel composites were prepared by in situ solvent-free radical bulk polymerization of methyl methacrylate (mma), after vacuum-assisted penetration of mma in aerogels. Compressive strengths and hardnesses were determined and found about 20-30% increase in strength as compared to the same batch of pmma samples without aerogel filler. The highest compressive strength values were approximately 120 MPa, which are similar to the strength values of cortical bones. Molecular weight distribution curves were determined by gel permeation chromatography and found very high peak values of approx. 2.5 MDa due to the nature of bulk polymerization.

Biocompatibility was tested by soaking the fresh fracture surfaces of aerogel composites (received after mechanical testing) in simulated body fluid (SBF) incubated at 37 °C for several weeks. Surface structure of samples before and after SBF treatments were examined by scanning electron microscopy. A dissolution of all aerogels from the pmma matrix had occurred during SBF treatment leaving porous structure behind, except for the heat treated silica aerogel, which performed very poorly, most likely due to the partial loss of surface silanol groups required for hydration and dissolution.

According to our results natural and functionalized silica aerogels seem to be promising candidates as lightweight, biocompatible fillers for pmma-based bone cements to increase their mechanical strength and improve surface tissue connectivity.

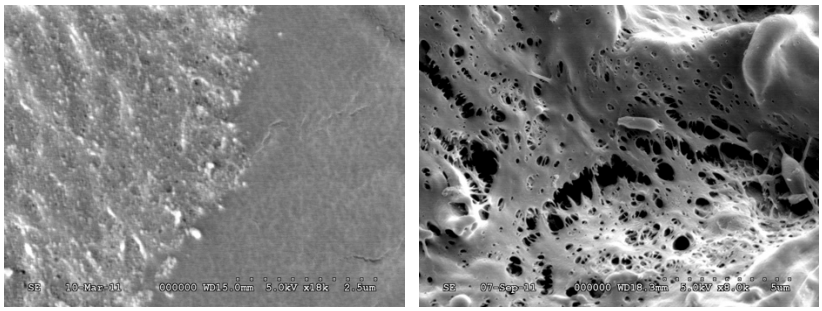

Fig. 1: SEM pictures of surfaces of a silica aerogel-PMMA composite before mechanical testing (left, 18k magn.) and after SBF treatment of fracture surface (right, 8k magn.).

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BEHAVIOR AND DAMAGE OF BIOCOMPOSITE MEMBRANES UNDER LARGE DEFORMATIONS

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Keywords: Membranes, biocomposite materials, free blowing, hyperelastic.

The numerical simulation of the processes of working of plastics (thermoforming, injection, stretching blowing) requires a good knowledge of the behavior of used materials. These materials are generally thermoplastic polymers (HDPE, ABS, PP…) heated between the temperature of vitreous transition and the temperature of melting to be then formed. However, the mechanical and rheological properties of new materials such as biocomposites are not enough elucidated in the literature. For this purpose, we are interested by the characterization of the behavior and the damage of the thermoplastic matrix biocomposites in free blowing.
From the experimental point of view, the experiments of free blowing of rubber membranes or polymeric circulars membranes are carried out as much at temperatures less high than those of working than at temperatures similar to those met in thermoforming and extrusion-blowing. For this kind of experiment, we can meet two approaches for the structural identification of mechanical or rheological parameters of the hyperelastic and viscoelastic membranes: i) that which use least squares algorithms and ii) that which uses neuronal algorithms.
The contribution aimed by this work is the hyperelastic identification of the parameters of a biocomposite membrane with a thermoplastic matrix (HDPE) reinforced by sawdusts, and the characterization of the rupture of these materials according to the pressure and the temperature.
Contrary to the structural hyperelastic models used in the literature to describe the behavior of thermoplastic membranes, we consider a Mooney-Rivlin model to describe free blowing of such biocomposites membranes. For this purpose, the technique of blowing of bubble is considered for the experimentation. For the identification, we use a neural algorithm (retro-propagation). For the phase of training, numerical results resulting from the modeling of the differential equations which govern the balance of the hyperelastic membrane are considered. The differential system is solved by the finite differences method with variable steps and differed corrections.

NOVEL BIOMIMETIC NANO-HYDROXYAPATITE/POLYMER COMPOSITE LOAD BEARING SCAFFOLDS FOR BONE TISSUE ENGINEERING

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Ceramic - polymer hybrid nanocomposites scaffolds have been considered as third–generation orthopedic biomaterials due to its close physical and chemical proximity with natural bone in comparison to first generation and second generation synthetic bone grafts [1]. Third generation nano-biomaterials, equipped with bioactivity and mechanical stability arising from the strength of nano-bioceramics in combination with flexibility and biodegradability of polymers, offer a promising approach for the issues concerning to bioactive bone grafting. Hybrid scaffolds also have the properties to stimulate specific cellular responses at the molecular level [2]. Numerous techniques and approaches to the development of three-dimensional scaffolds have currently been reported in the literature. Among all the processes of scaffold synthesis, matrix mediated biomimetic route is most promising one. However, biomimetically synthesized scaffolds are reported to be useful for non-load bearing applications.

Extending the concept of biomimetic for load bearing applications, the synthesis of a novel polymer based three dimensional hydroxyapatite (HA) nanocomposites scaffolds have been demonstrated and discussed in the present study. The biomimetic nanocomposites scaffolds are synthesized by *in situ* nucleation and growth of HA nanoparticles in a preorganized carbomethoxycellulose (CMC) matrix at ambient temperature, followed by a thermally induced gelation of the system at 50 ^{o}C, resulting a three dimensional macro/micro porous scaffold (Fig.1). The structural characterizations of the scaffolds are carried out by Scanning electron microscope, Fourier transform infrared spectroscopy, Atomic Force Microscopy, Transmission electron microscopy and mechanical test. The mechanical compressive strength of the scaffolds measured by Universal mechanical testing Machine is in the ranges of 40-50 MPa and an elastic modulus136-225 MPa. The microstructure of the scaffolds obtained by SEM (Fig.2) revealed the interconnecting irregular pores between 0.005 μM to 110 μM formed by self assembled HA nano particles (100 nm - 150 nm) nucleated in the polymer matrix. Bioactivity studies confirmed cytocompatibility of the scaffolds to the bone marrow driven mesenchymal stem cells (BMSC). Paper will also include a compositional dependence of mechanical properties of the scaffolds as well as cell-material interaction.

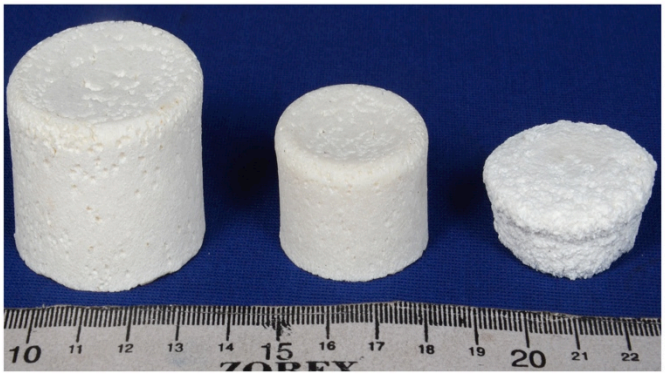

Fig.1 3D nano-composites scaffolds

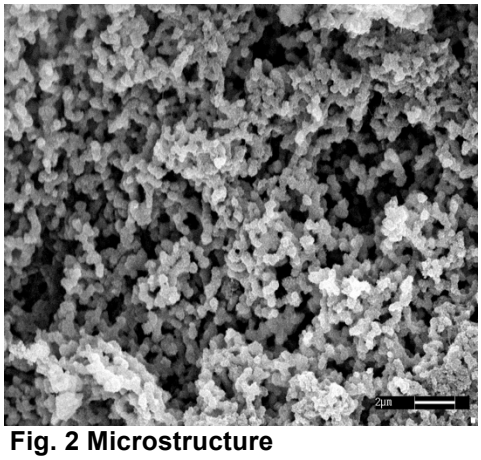

Fig. 2 Microstructure

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EXTRUSION OF NANOCOMPOSITES REINFORCED WITH CELLULOSE NANOWHISKERS, USING PEO AS ADSORBED POLYMER

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CNW (cellulose nanowhiskers) have attracted significant attention because they are renewable and environmentally benign, naturally abundant, biodegradable, biocompatible and have excellent mechanical properties. Incorporation of nanocrystalline cellulose suspension (NCC) in polymeric matrix systems results in nanocomposite materials with improved mechanical properties. The main problem for the preparation of these nanocomposites is related with the heterogeneous dispersion of NCC within the polymer matrix, due to the main interactions between CNW.

Thus, the objective of this work is to improved dispersion/compatibilization of CNW (from cotton cellulose) in a polymeric matrix by using and adsorbed polymer, with the final aim to prepare cellulose nanocomposites by melt-extrusion techniques.

For this research, polyethylene oxide or “PEO” was chosen to functionalise the surface of the cellulose nanowhiskers. Theory predicts that the PEO adsorbs onto the surface of the cellulose nano-whiskers by means of hydrogen bonding. In a PEO and CNW suspension, this adsorption phenomenon can be observed by a change in viscosity. There is a minimum value of viscosity at which theoretically all of the PEO has adsorbed onto the cellulose nanowhiskers. After this minimum value, the viscosity begins to increase due to excess CNW. This theory is further explored throughout this work, examining how the saturation point varies with PEO molecular weight and cellulose nanowhisker concentration.

The influence of the nature and molecular weight of the PEO (from 35.000 to 5.000.000) on the extrusion capability of the nanocomposite, and on its morphological and thermo-mechanical properties is also studied.

From these experiments, interesting results were observed, from which it was possible to determine an optimum CNW concentration at which all the available PEO chains are adsorbed on to the surface of the nanoparticles. Using this experimental data, low density polyethylene (LDPE) was extruded with PEO functionalized CNWs. By using PEO as a compatibility agent for the CNWs, both improved dispersion in LDPE and thermal stability were observed.

DEVELOPING A HIGH-STRENGTH GIC FOR IMPROVED DENTAL RESTORATIVES

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Glass-ionomer cements (GICs) have been successfully applied as dental restoratives for more than 29 years [1]. An acid-base reaction between calcium and/or aluminum cations released from a reactive glass and carboxyl anions pendent on polyacid describes the setting and adhesion mechanism of GICs [2]. Much effort has been made to improve the mechanical strengths of conventional GICs. Light-cured GICs (LCGICs) are improved resin-modified GICs with reduced moisture sensitivity, improved mechanical strengths, extended working time and ease of clinical handling [3]. Redox-initiated GICs have also shown attractive properties such as improved mechanical strengths and controllable curing time [4]. The strategy of increasing MW of the polyacid by either introducing amino acid derivatives or N-vinylpyrrolidone has also shown enhanced mechanical strengths [5-6]. The objective of this study was to synthesize and characterize a new hyperbranched poly(acrylic acid), use the polymer to formulate the cements with glass fillers, and evaluate the mechanical strengths of the formed cements.

Synthesis of the hyperbranched poly(acrylic acid) followed the procedures described elsewhere [7]. The initiators and polymers were characterized using FT-IR and NMR. The reaction kinetics was investigated. The effects of arm number and branching were studied as well. A two-component system (liquid and powder) was used to formulate the cements. The liquid was made by simply mixing the synthesized polymer with distilled water at a ratio of 70/30 (by weight). Commercial LCGIC Fuji II LC glass powder was used to formulate the cements with a powder/liquid (P/L) ratio of 2.7/1. Fuji II LC was used as control. Specimens were prepared in different molds for the corresponding mechanical testing. After blue-light curing, the specimens were conditioned in distilled water at 37 ^{o}C for 24 h prior to testing. Compressive strength (CS), diametral tensile strength (DTS), flexural strength (FS), fracture toughness (FT), Knoop hardness number (KHN), attrition and abrasion tests were used to evaluate the mechanical properties of the formed cements. One-way analysis of variance (ANOVA) with the post hoc Tukey-Kramer multiple-range test was used to determine significant differences of the measured properties among the materials in each group. A level of $\alpha = 0.05$ was used for statistical significance

The results showed that the experimental cement formulated with the newly synthesized hyperbranched polymer exhibited significantly higher mechanical strengths than commercial Fuji II LC. The experimental cement was 53% in CS, 50% in compressive modulus, 125% in DTS, 95% in FS, 21% in FT and 96% in KHN higher than Fuji II LC. The experimental cement was only 5.4% of abrasive and 6.4% of attritional wear depths of Fuji II LC in each wear cycle.

It appears that this novel experimental cement is a clinically attractive dental restorative and may potentially be used for high-wear and high-stress-bearing site restorations.

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L-DIPHENYLALANINE ASSEMBLIES AS POTENTIAL CARRIERS FOR DRUG DELIVERY

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Biomaterials based on self-assembly of biological building blocks have emerged as a promising alternative for the production of drug carrier systems, with greater biocompatibility and specificity in cell recognition.[1] One of the simplest and most widely used building blocks is L-diphenylalannine (FF). FF self-assembles into a variety of nanostructures with 1-D arrays; the most commonly found FF nanostructures are nanotubes, nanoribbons and nanowires.[1] Particularly, FF tubular arrangements exhibit six FF residues forming a hexamer structure.[2] These units interact through hydrogen bonding and π-π stacking of aromatic residues, forming a porous matrix with hydrophilic channels parallel to the long axis. The external wall of the tubes has been characterized as very hydrophobic where as the inner core has been found to have both hydrophilic and hydrophobic properties. These characteristics make them very interesting vehicles for vectorization because they enable the loading with macromolecules of different degrees of hydrophobicity.

In this work, we have conducted investigations on the potential of FF tubular arrays (FF-NTs) for the transport of medication. Rhodamine B (RhB) was chosen as a model drug mainly due to the traditional use of this molecule as biological marker for fluorescence assays. Moreover, its hydrophilic nature allows the incorporation in the inner core of the assemblies, which is a suitable condition to protect the load against damages from the contact with the surrounding medium. Besides, we have investigated the cell toxicity of these nanomaterials, and its potential as a drug delivery system.

The evaluations of the FF-NTs toxicity were made initially *in vitro*, using mouse erythrocytes as a model cell in presence of different concentrations of FF-NTs, by monitoring the release of hemoglobin in the erythrocyte membrane at 412 nm. The results indicate that the saturation concentration and solubility of the membrane were equal to 1.9 mg mL-1 and 4 mg mL-1, respectively (Fig. 1A). On the other hand, cell viability test were made by reduction of the 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) dye on culture of mouse fibroblast cells, using different concentrations of FF-NTs (0.01-5 mg mL-1). The results demonstrate FF-NTs stability until 0.25 mg mL^{-1} and total lysis in approximately 1 mg mL-1 (Fig. 1B). The evaluation of FF-NTs as carrier for drug delivery system was also obtained by incorporation of RhB (Fig. 1C). In this case, the permeability measurements were realized with and without RhB (1mM) into FF-NTs. We have observed that the constant release of RhB when adsorbed inside FF-NTs is slower (8.13±1.05 $\mu g.mL^{-1}.min^{-1}$) when compared with RhB only (46.63 ± 14.5 $\mu g.mL^{-1}.min^{-1}$). The data indicate a possible haemolytic use of FF-NTs carriers in small concentrations, which is excellent especially for intercalation or complexation of hydrophilic compounds.

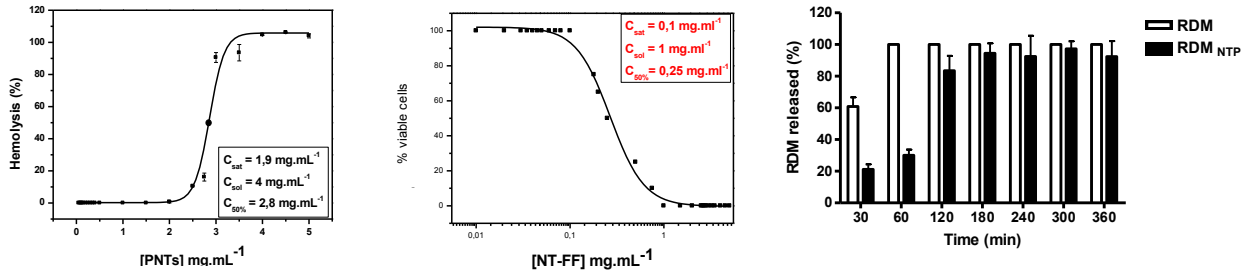

Fig. 1: (A) hemolytic effect of FF-NTs in erythrocytes; (B) cytotoxic effect of FF-NTs in fibroblasts, and (C) liberation of Rh B incorporated in the FF-NTs.

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Acknowledgment: FAPESP, UFABC, LNLS, INCTBio, CNPq and CAPES

SELF-ASSEMBLED DIPHENYLANINE MICRO/NANOTUBES PREPARED VIA SOLID-VAPOR PHASE[1]

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The short aromatic dipeptide L-diphenylalanine (FF) was used to build supramolecular assemblies from amorphous films deposited onto Si substrates, Figs. 1-A and B, by using an adapted form of the solid-vapor method recently proposed by Park et al. [2]. This approach has been successful in obtaining extense vertically-oriented nanoforests [3]. Unlike the studies reported elsewhere, we have conducted our experiments under atmospheric pressure, which is presumably ideal for further large-scale production. The formation of the structures was examined under different preparation conditions; specifically, the nature of the solvent (water or aniline), the concentration of peptides in the precursor solution and the incubation time were varied. Our results indicate that changes in preparation have dramatic consequences on the final morphology of the assemblies. Particularly, we find the formation of vertically-oriented nanofibers, but here they appear confined in clusters when the samples are incubated under water vapor (Fig. 1-D). Interestingly, when aniline vapor is used, we observe that the methodology allows the formation of micrometric tubes lying on the surface and gives rise to homogeneous peptidic networks across the substrate (Fig. 1-F). Spectroscopic data reveal that different vapors promote the emergence of new vibrational modes, which is interpreted as a change in the symmetry of the molecular arrangement that is accompanied by an increase in the number of degrees of freedom. These findings strongly indicate that different symmetries,presumably orthorhombic and hexagonal symmetries, can be obtained depending on the type of solvent used during the preparation. To assess the interaction between our structures and a functionalizing agent, and get some insight on future applications in sensing architectures, aniline was polymerized onto the structured films and then their morphological and spectroscopic behaviors were also investigated.

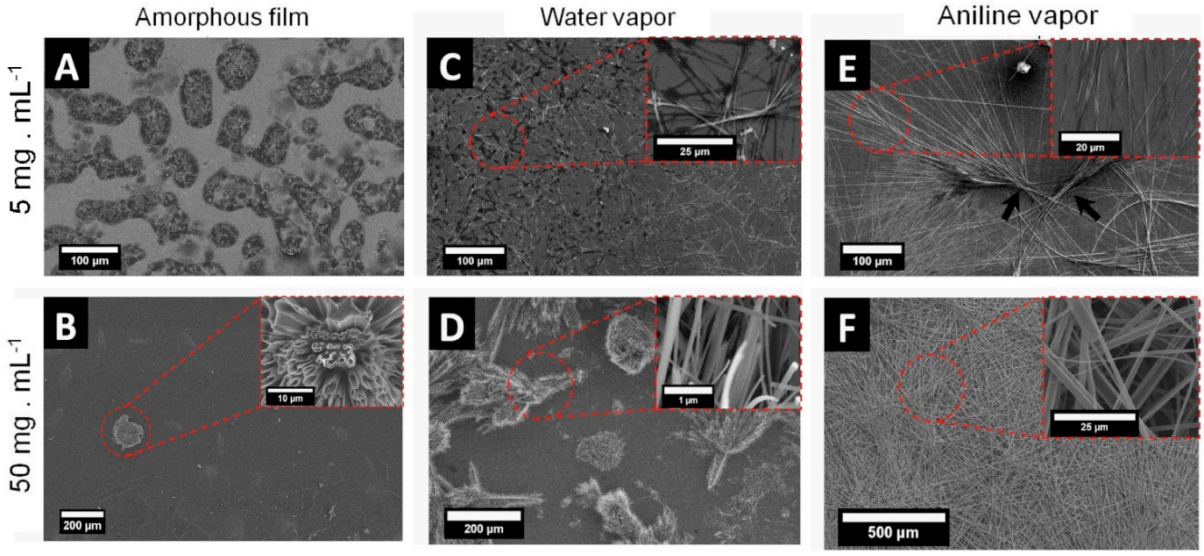

Fig. 1: SEM images showing the morphology of structures grown onto Si substrates.

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Acknowledgment: UFABC, FAPESP, CNPq, CAPES and INCTBio.

PHASE BEHAVIOUR, STRUCTURE AND KINETICS OF SELF-ASSEMBLIES OF COLLOIDAL ROD-LIKE *FD* VIRUSES BY DEPLETION INTERACTION

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Viruses have been highlighted as new building blocks for the self-assembly of organized materials. [1] Colloidal rod-like *fd* viruses, semiflexible filamentous bacteriophages with chiral arrangements of capsid proteins, can self-organize into liquid crystalline phases which coincide with the theoretical predictions, because of their uniformity in size making them a model system in soft condensed matter. [2] In pure rod suspensions, they form stable isotropic, chiral nematic, smectic, columnar, and crystalline phases by increasing rod concentration, with repulsive short-range interaction between the viral particles. [3] Nevertheless, in the mixtures of the rod-like *fd* viruses and the non-adsorbing polymers, the crowding of the polymers induce an effective attractive interaction between the rods due to the imbalance of osmotic pressure, which is called depletion attraction. [4] This entropy-driven long-range attraction induces phase separation [5] and the *fd* viruses self-assemble into well-defined micro-objects such as membranes, tactoids, bundles, and ribbons. [2,6] In this presentation, we establish a phase diagram of different observed structures depending on the concentrations of rod and polymer. Then, we correlate the continuous change of the self-assembled morphologies (membrane, micro-disk, and bundle) and their corresponding internal structures (hexagonal packing with different inter-rod spacing) as varying polymer concentration, by using optical microscopy and small-angle X-ray scattering. Finally, we reveal the kinetic mechanism of the membrane growth by using video microscopy, and analyse their internal structure in particular the presence of intrinsic dislocations.

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NANOSTRUCTURED MAGNETIC MATRIX FOR THE STUDY OF INTRACELLULAR MECHANISMS OF BIOMINERALIZATION

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In nature, magnetotactic bacteria synthesize intracellular mineral magnetic nanoparticles. This biomineralization process is a mechanism that has shown great potential to inspire bottom-up material syntheses. To understand the effect of magnetic field on the growth of magnetic biogenic nanoparticles, encapsulation of bacteria in a silica metal-oxide nanoparticles matrix has been performed.

For the design of magnetic gels via the sol-gel process, magnetite nanoparticles (Fe_3O_4) have been synthesized in liquid polyol in mild conditions. The morphology, size and the structure of nanoparticles were studied using TEM and XRD. These nanoparticles are monodisperse with a size range between 10 and 16 nm.

The formation of magnetic gels is obtained after the homogeneous dispersion of magnetite nanoparticles within a solution of sodium silicate. The acidification of the mixture led to a magnetic cytocompatible gel.

To evaluate the cytocompatibility of the matrix, *E.coli* bacteria were encapsulated within magnetic gel in the absence of nutrients. Viability tests were performed using plate-count technique which gives the number of culturable bacteria. Directly after the encapsulation in the magnetic gel, 60*% of E.coli* bacteria are still viable/culturable.

BIOINSPIRED NANOTECHNOLOGY: FROM $CaCO_3$ BIOMIMETIC CRYSTALLIZATION TO OVERBASED NANODETERGENTS PREPARATION

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The phase transformation of calcium carbonate ($CaCO_3$) is of extensive concern since $CaCO_3$ serves both as the most abundant biomineral in nature and an important industrial filling material [1].

Functional hyperbranched (hb) polyesters or polyglycerols were synthesized and employed as crystallization modifiers of $CaCO_3$, replacing biomacromolecules involved in biomineralization, to mimic the formation of the advanced biomineral materials. It is found that selectivity for certain crystal faces in modified inorganic crystals appears to be highly dependent on the secondary structure of the macromolecule additives [2]. The as-prepared $CaCO_3$ mediated by the functionalized hb polymers was narrow distributed uniform spherical particles in metastable vaterite polymorph (Fig. 1A and 1B).

Based on the knowledge of polymorph and morphology control of $CaCO_3$ from experience in the research practice on biomimetic crystallization, industrially valuable overbased nanodetergents from calcium salt of heavy alkylbenzene sulfonate have been successfully prepared by optimizing preparation conditions (Fig. 1C and 1D) [3]. For further probing into the mechanism of this complex process, some simple sulfonates have recently been employed as model surfactants, such as dodecylbenzene sulfonate and tetracosylbenzene sulfonate, for the carbonation process investigation and nanodetergents preparation. A phase transformation from amorphous calcium carbonate (ACC) into the vaterite polymorph during the overbasing reaction has been unambiguously demonstrated (Fig. 1E, 1F, 1G and 1H). This mechanism understanding may be of crucial importance for the preparation and quality control of lubricant additives and greases.

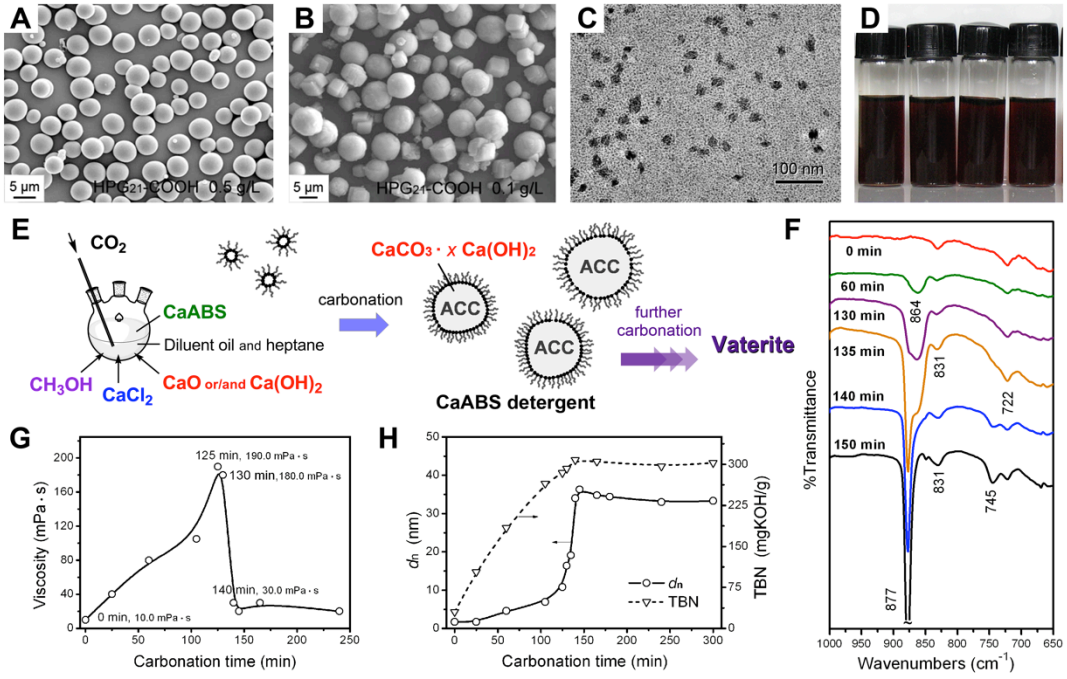

Fig. 1: Applying the knowledge of biomimetic polymorph and morphology control of $CaCO_3$ (A,B) into the mechanism investigation and preparation of high quality overbased calcium alkylbenzene sulfonate nanodetergents (C, D, E, F, G, and H)

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FORMATION OF CaCO3 NANOSTRUCTURES INDUCED BY NACREOUS ORGANIC EXTRACTS

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Biomimetic $CaCO_3$ crystals are produced by adding the soluble organic content of the nacreous layer of *Pinctada margaritifera* pearl oyster to a supersaturated solution of calcium carbonate [1]. For SOM amounts higher than 25 ppm, the synthesized calcitic crystals exhibit two main structural features of nacre: a *hierarchical structure* characterized by locally stacked planar mineral layers and a *nanostructuration* of these layers. AFM and electron microscopies supplemented by FTIR spectrometry allowed us to demonstrate that each layer is actually composed of packed nanograins embedded in an organic matrix. Moreover, each layering plane exhibits a single crystal character under TEM and SAED characterizations, and can be indexed to the {110} planes of calcite. This suggests that crystal growth may occur by an oriented aggregation of mineral nanoparticles, stabilized by organic molecules. It clearly demonstrates the specific role of the nacreous soluble organics in inducing a nanostructuration of the crystals, a feature which is moreover common to all calcareous biocrystals [2].

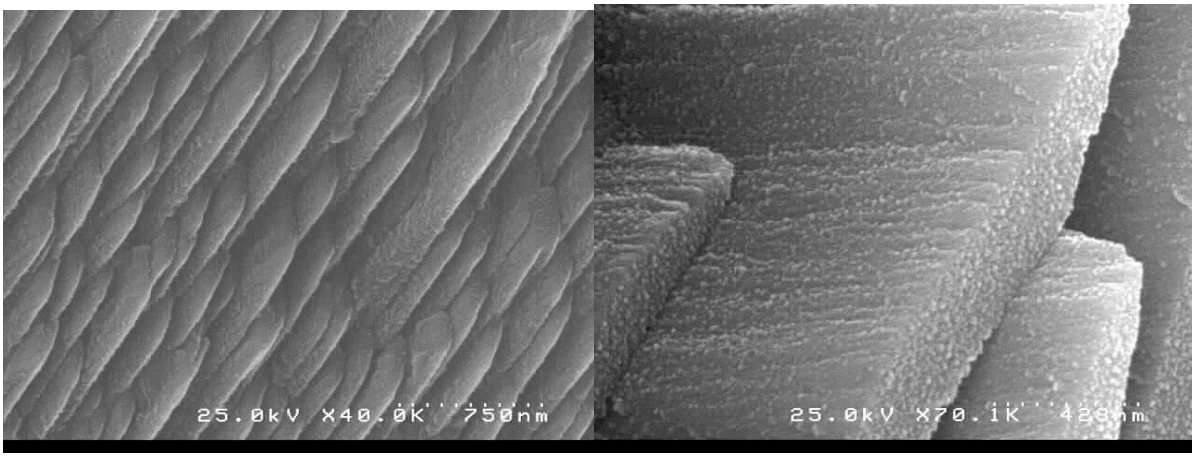

Fig. 1: SEM images of $CaCO_3$ crystals produced by adding 100 ppm of soluble organic extract of *Pinctada margaritifera* nacre to a mineralizing solution. One can see both the stacked mineral layers (left image) and the nanostructuration of each layer (right image).

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BIOMIMETIC MINERALIZATION OF POLYMER FIBER MAT CROSS-SECTIONS

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Biomimetic mineralization methods can be used to coat different calcium phosphate (CaP) phases on polymeric fibers which are promising in bone tissue engineering. Mineralized fiber surfaces provide a superior medium for cell adhesion, spread and growth compared to bare surfaces [1-6].
Synthetic body fluids (SBF) which are generally formulized such that they resemble the mineral constituents of the blood plasma have been widely used to form biomimetic coatings on different substrates. Concentrations of the constituents of SBF recipes can be multiplied to increase the deposition rates. 10×SBF has the advantage of decreasing the deposition durations to less than 6 h and eliminating the need for buffering agents [7]. Different calcium phosphate phases can have different dissolution rates in the body environment depending on their phase constitution. A phase mixture that would provide variable dissolution rate is generally accepted to be more beneficial in tissue engineering approaches. When used with polymeric fibers, 10×SBF results in coatings that are composed of a mixture of two distinct calcium phosphate phases, namely dicalcium phosphate dihydrate (DCPD-brushite) and calcium deficient hydroxyapatite (CDHA) [1,2,6]. The modified 10×SBF recipes with less phosphate source or more bicarbonate source were observed to deposit a morphologically different mixture of DCPD/CDHA or only CDHA, respectively [6]. On the other hand, concentrated SBFs are prone to bulk precipitation rather than heterogeneous nucleation on the scaffold surfaces [8], and the dense, rapidly forming initial coating on the surfaces does not permit the coating solution to infiltrate through the cross-section. Therefore the fibers deep in the cross-section remain uncoated. The generally applied biomimetic technique needs to be modified also for more sophisticated 3D construction methods that are yet to be matured.
In this study, in order to initiate a supersaturation within the cross section and surfaces of the mats simultaneously, constituents of SBFs were divided into two by the fibrous mat to be coated. Possible ways that could be envisioned in division of constituents were narrowed down with the thermodynamic model used (Figure 1). Supersaturating the two sides of the mats with respect to different CaP phases allowed also the formation of phase mixtures in the cross-sections of the membranes.

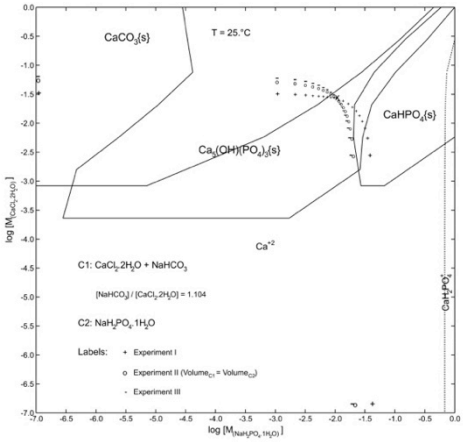

Fig. 1: Calculated phase stability diagram; calcium/bicarbonate sources in one compartment (C1) and phosphate source in the other (C2)

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FUNCTIONALIZED MULTIWALLED CARBON NANOTUBES AS TEMPLATES FOR CRYSTALS GROWTH OF CALCIUM CARBONATE

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Biomineralization is the process by which living organisms exert control over minerals they deposit, creating materials with remarkable morphologies and advanced properties [1]. Several approaches have been explored including the effect of different templates and/or additives on *in vitro* crystallization of calcium carbonate ($CaCO_3$), the major mineral component of exoskeleton of many animals. Many of these templates in the form of films, spheres, sponges, ligand receptor complexes, block copolymers, polypeptides and grafted polymers have been used to synthesize specific crystalline forms. On the other hand, carbon nanotubes (CNT) represent versatile materials with advanced properties useful in many applications such as biomedicine, nanotechnology, electronics, optics, and other fields of materials science. Nowadays, two main obstacles exist to overcome in using CNT as template for biomineralization: the hydrophobic character and the chemical inertness. Tasis *et al*. reported the use of MWCNTs grafted with poly(isoprene-*b*-acrylic acid) amphiphilic copolymer as template for crystallization of $CaCO_3$, where spherical or ellipsoidal calcite nanocrystals were obtained [2].
This research was motivated by scarcity of publications on the effect of CNT for the control of $CaCO_3$ crystallization. Herein, we evaluated the influence of oxidized and functionalized MWCNTs on $CaCO_3$ crystallization using gas diffusion method. Unmodified MWCNTs were Baytubes® 150 CP from Bayer, Germany. Oxidation of MWCNTs was carried out in a mixture of 2:1 HNO_3: H_2SO_4 by refluxing for 1 h, followed by washing with water and drying. Functionalized MWCNTs with itaconic acid (IA) or monomethylitaconate (MMI) were obtained by direct esterification of oxidized MWCNTs with IA or MMI, respectively. The insertion of carboxyl and hydroxyl groups on the surface of functionalized MWCNTs was confirmed by FTIR analysis. The mmorphological aspect and the agglomeration of MWCNTs were observed by TEM. The oxidized MWCNT induced selectively the formation of aragonite crystals, while modified and truncated calcites were obtained with MWCNTs functionalized either with IA or MMI. In addition, fluorescent MWCNTs obtained with Fluorescein-5-thiosemicarbazide (5-FTSC) molecules was used to visualize functionalized MWCNTs adsorbed on the $CaCO_3$ crystal surface. TEM, FTIR/ATR, XRD and Raman analyses of the $CaCO_3$ particles are in progress. We have demonstrated that functionalized MWCNTs can control the morphogenesis and polymorphism of $CaCO_3$ crystals. In summary, functionalized CNTs as template offer a good alternative for CNT-controlled crystallization and a convenient approach for understanding the biomineralization process useful for the design of novel hybrid materials.

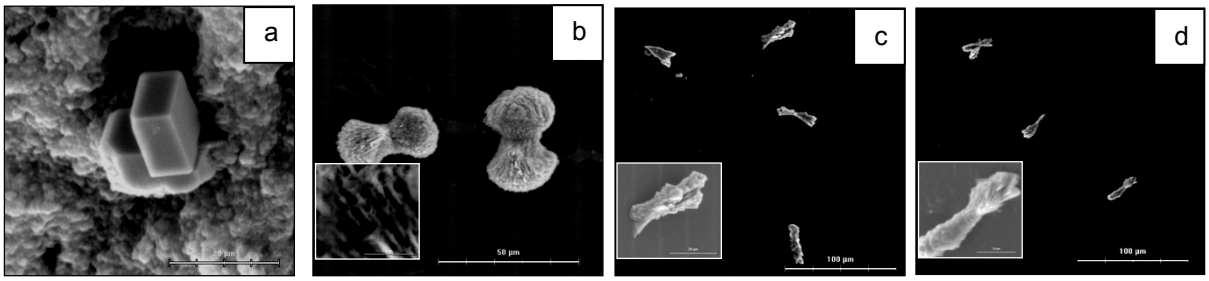

Fig. 1: SEM images of $CaCO_3$ crystals grown in the presence of: a) MWCNT, b) oxidized MWCNT (MWCNT-Ox) c) functionalized MWCNT with IA, d) functionalized MWCNT with MMI.

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BIOMIMETIC HYDROXYAPATITE NANOCRYSTALS FOR BIOMEDICAL AND ENVIRONMENTAL APPLICATIONS

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The synthesis of inorganic and organic-mineral hybrid nano-particles, inspired by the processes of biomineralization that occur in ambient conditions, is the main goal of our research activity. These synthetic biomimetic nanostructured materials mimick biological ones in composition, structure, morphology, surface area and bio-reactivity have enhanced properties in term of mechanical, optical, magnetical and capability in responding to biological environment features and stimuli [1].
Our research has been addressed mainly to the design of synthetic strategies, with the possibility of a scale-up, capable of producing nanometer-sized particles of calcium phosphates hosting (macro) molecules of biological and environmental interest [2] or producing biomorphic scaffolds for tissue engineering [3].
The functionalization of these nanoparticles will occur both onto surface and into the bulk. This double approach will allow to have materials with different capability to response.
These nano-materials will be able to specifically recognize biological substrates superficially interacting with them, like enzymes, or to release their entrapped molecules into specific environments, like cellular surfaces. Contemporary these nano-materials will be able to entrap on the surface and in bulk organic molecules and metallic ions respectively which are toxic for the environmental biological system and human health.

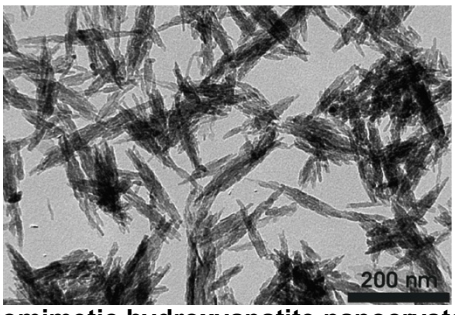

Fig. 1: Synthetic biomimetic hydroxyapatite nanocrystal for drug delivery

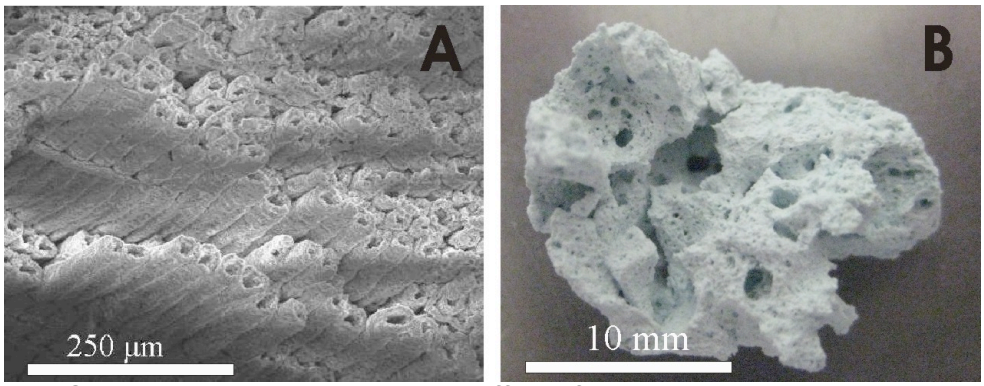

Fig. 2: Synthetic biomorphic apatitic scaffolds from wood a) and sea sponges b)

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STRUCTURAL INVESTIGATION OF MULTICOMPONENT ORGANIC SYSTEMS USING X-RAY AND OPTICAL TECHNIQUES

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The organic layered systems are very promising objects in the development of biosensors, photovoltaic elements, biomedical investigation etc. It is possible to design biomembrane models in the form of the planar organic systems consist of complex mixture of lipids and proteins. Langmuir-Blodgett (LB) technique is common way to prepare multicomponent organic systems on the water subphase or solid substrate. The structural studies of biomembrane models provide information about self-organization phenomena in biomembranes and their functional properties.

It is perspective to use combination of X-ray and optical techniques (X-ray standing wave technique, X-ray reflectivity, Brewster microscopy) for structural investigation different multicomponent organic systems on liquid subphase (Langmuir monolayers) and on the solid substrate (Langmuir-Blodgett films). Brewster Angle Microscopes (BAM) enables to observe the formation of a monolayer at the air-water interface using a Langmuir trough. It provides information on homogeneity, phase behaviour and film morphology. X-ray reflectivity (XRR) and X-ray standing wave technique (XSW) are widely used for indestructible structural characterization various organic and inorganic thin layered systems [1-3]. XRR provides information about the electron density profile normal to the surface and it can be used to determine various properties of a thin film and interfaces: thickness, density, roughness. XSW based on simultaneously measurements of X-ray reflectivity and X-ray fluorescence yield angle dependences. The XSW allows to determine the distribution of the different kind of atoms normal to the surface.

In present work we applied this approach for research of multicomponent organic systems: fat acid monolayers on the liquid subphase with metal ions, lipid-protein system, multilayers LB films. Study of self-organization of such systems on the liquid surface, features of the formation and restructuring of the LB films were carried out.

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SCAFFOLDS MADE OF RECOMBINANT SPIDER SILK PROTEINS OPTIMIZED FOR BIOMEDICAL APPLICATIONS

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Spider silk proteins show good biocompatibility and a weak immune response. [1] Therefore they are desirable polymers for biomedical applications. In the past we have developed a strategy to produce and purify designed recombinant spider silk proteins based on major ampullate spidroins of the dragline silk of the European garden spider *Araneus diadematus.* [2] These recombinant silk proteins can be processed into various morphologies, e.g. films and non-wovens among others, useful for biomedical applications such as wound dressings, implant coatings or as scaffolds in tissue engineering. [3]

For certain applications a good adherence of cells to material surfaces is of great importance. We could show that there is only weak cell attachment on flat films made of the native-like spider silk protein eADF4(C16) due to low physical or chemical interactions between the cells and the surface. These interactions were improved by morphological changes of the silk scaffolds. [4]

Further, we have employed specific chemical and genetical modifications to improve interactions of cells with the silk surface on a molecular level. Adjusting the morphological as well as the molecular properties of a silk scaffold results in improved cell adhesion and faster cell proliferation.

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INVESTIGATION OF SURFACE PROPERTIES OF NANO-STRUCTURED TiO_2 FOR DENTAL IMPLANTS DESIGN

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The objective of this work is to study the influence of physico-chemical characteristics of TiO_2 nanotubes on their interaction with biological molecules or cells, and study specific adsorption properties of these nanostructures to better understand and optimize their ability to be functionalized, which may optimize the osteointegration process of the dental implants.

Methods: Titanium nanotubes arrays were fabricated by anodic oxidation of titanium samples in a fluoride-based solution . TiO_2 nanotubes surface have been functionalized with hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and doped hydroxyapatite by Strontium using a pulsed electrodeposition process. The samples were characterized primarily by IR,XPS DRX and next by scanning electron microscopy (SEM). The ability of such surfaces to adsorb selected biomolecules at solid-liquid interface have been studied. Amino acids and larger biomolecules adsorption have been studied by FTIR spectroscopy.

Results: The nanostructuring of the surface of titanium can be optimized by chemical or electrochemical treatment . The creation of new surface sites allows to get specific reactive sites on TiO_2 nanostructured surfaces. These sites are points of "attachment" to a privileged bioactive coating formed of hydroxyapatite. A partial substitution of Ca^{2+} doped by Sr^{2+} was used to increase the cell growth mechanism, with a perspective study of a biological test of cells growth on the nanotubes of TiO_2.

Conclusion: We can create surfaces which have a controlled nano-topography and modified chemistry to promote biological interactions. Ongoing studies allow us to discover the influence of these changes on the adsorption of bio-molecules (amino acids, proteins) and cells for optimal osteointegration.

BIOINSPIRED SKIN TISSUE BIOMATERIAL

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Skin is the largest organ in the human body. The demand for skin tissue and wound dressings has increased drastically in the last 2-3 decades mostly because of illness and injuries caused by transport accidents (i.e. cars, aircrafts and buses crashes) and fire accidents resulting in severe burn damages [1-3]. Therefore, the development of new viable alternatives is needed based on biomaterials and skin-tissue engineering [1-3]. Emerging dressing types include interactive/bioactive dressings and tissue-engineered skin substitutes. Nevertheless, there is no one dressing that is suitable for the management of all types of chronic wounds and few are suited for the treatment of a single wound during all stages of the healing cycle. Successful wound management depends on an understanding of the healing process combined with knowledge of the properties of the various dressings available. In the present study it is developed a new hybrid system based on water soluble synthetic polymer and chemically modified carbon nanotubes. Specifically, the hybrids were produced by dissolving polyvinyl alcohol (PVA) in water and adding carboxylic functionalized multi-wall carbon nanotubes (CNT-COOH). So, membranes were produced from the dispersion by solvent-casting procedure at room temperature. The results have indicated that the nanocomposite membranes were obtained with thickness, mechanical properties and swelling behavior similar to those characteristic of skin tissues. Moreover, these designed hybrids have also presented preliminary biocompatibility based on the response of cell cultures using MTT assay (tetrazolium compound). In that sense, the novel nanostructured hybrids could be considered as a promising biomaterial to be potentially used as wound cover or matrices for tissue repair and regeneration in several biomedical and tissue engineering applications.

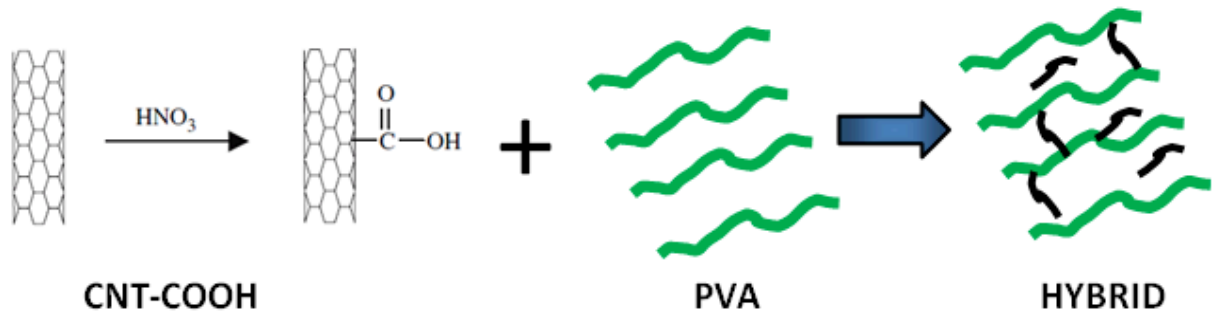

Fig. 1: Synthesis of the hybrid nanostructure.

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SURFACE BIOMIMETICS OF OSMOTIC ADOPTION

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Osmotic adoption of microorganisms found in biotopes like salt lakes, salt mines, salinas, and other sites of elevated salinity requires osmotic equilibrium across the membrane. One strategy of osmoadoption, widely spread among halophilic eubacteria, involves production and accumulation of neutral non-ionic organic molecules of low molecular weight. These compounds (e.g. ectoine) do not interfere with the cell´s metabolism even at concentrations well above 1M, and are assigned potential for various technological applications. At the molecular level, the mechanism of their action is not known. We have mimicked and studied the interaction of ectoine with surface tethered DNA and its influence on the DNA bioactivity (hybridisation, complex formation with g5p protein) with a variety of methods (surface plasmon resonance, confocal fluorescence, AFM, Raman). The data provide the bases for the discrimination between the existing models of the osmoprotection.

FORMATION OF NANOPILLARS OF SILICON

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In recent years, much effort has been made for the manufacture of one dimensional nanostructured materials for use in nanodevices. Silicon is a basic material in microelectronics, especially nanowires and silicon nanopillars. Both of these nanostructures have attracted much attention for their application as nanoscale biosensors.
Recently, a promising way to fabricate such structure is to cover a crystalline silicon substrate with mono disperse nanosized objects, which subsequently are used as a mask for silicon etching. The next interesting step of progress was made when silicon pillars were synthetized in a form of highly ordered two-dimensional arrays using the advances of nanosphere lithography.
In this work we report the fabrication of highly ordered array pillar silicon by a simple chemical etching of silicon in vanadium oxide/fluorhydric acid solution. Different etching parameters including the solution concentration, temperature and orientation of Si substrates and thin metal catalyst film deposition (Pd) on the Si surface were studied. The etched surfaces characterized by Scanning Electron Microscopy and Spectrophotometry are shown on fig.1 . It has been found that the morphology depends on both etching time and the presence of the catalyst. The results show a different morphology in each case. As shown in the figure below, the attack, on the surfaces with a Palladium deposit, begins by creating pores on palladium in which we distinguish the formation of pyramid structure which means the creation of nanowires of silicon.
Finally, taking into account the obtained results, a mechamism of the chemical etching is proposed.

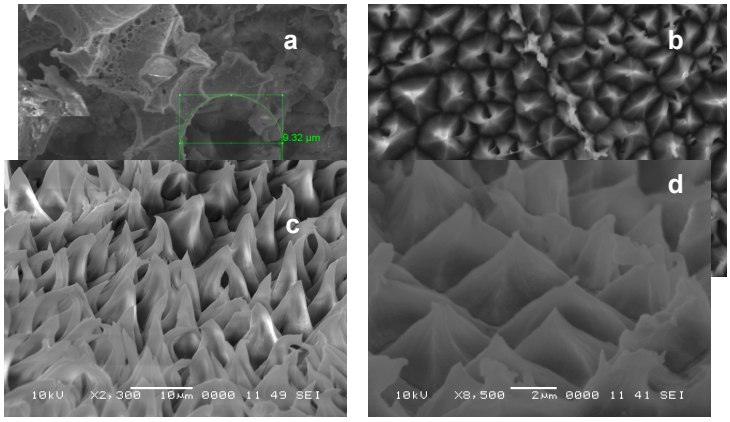

Fig. 1: SEM pictures of silicon on HF/V_2O_5 solution
a) [2]Silicon with Pd deposit, b)[3] Only silicon, c)[3] and d)[3] cross section of b)

MODELLING INVESTIGATION OF 1-D And 2-D METAMATERIAL LENS

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A novel microwave nondestructive evaluation (NDE) sensor was developed in an attempt to increase the sensitivity of the microwave NDE method for detection of material defects small relative to a wave length.
The sensor was designed on the basis of a negative index material (NIM) lens. Transmission at the resonant frequency through the 1-D lens was determined to be about 10 times higher than that with the 2-D lens.
However, the focusing ability of the 1-D lens was found to be slightly lower to the 2-D lens (focus spot size for the 1-D lens was determined to be 0.7λ vs. 0.48λ for the 2-D lens). A fiberglass material sample with a 3mm (0.037λ) diameter through hole (perpendicular to the propagation direction of the wave) was tested with both lenses.
The hole was successfully detected with an 8.2 cm wave length electromagnetic wave with both lenses, but the image obtained with a 2-D lens was much sharper. Therefore, the choice of the lens to be used in a sensor is prescribed by the specific requirements of the testing system.
For example, a 1-D lens should be considered when the simplicity of the testing system is deemed more important than the quality of the image obtained from a defect. A 1-D lens also allows for a longer sample standoff distance and higher transmission.

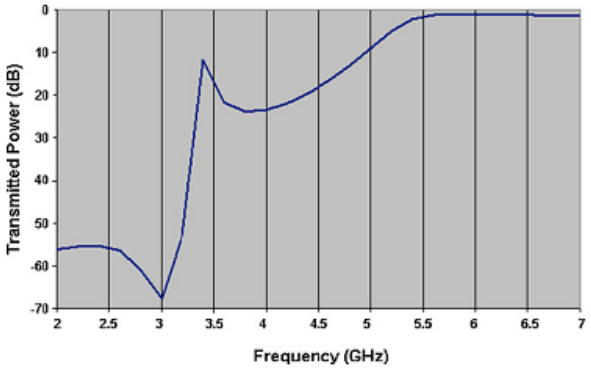

Fig. 1: Modeling results for transmitted power as a function of incident microwave frequency for 1-D lens

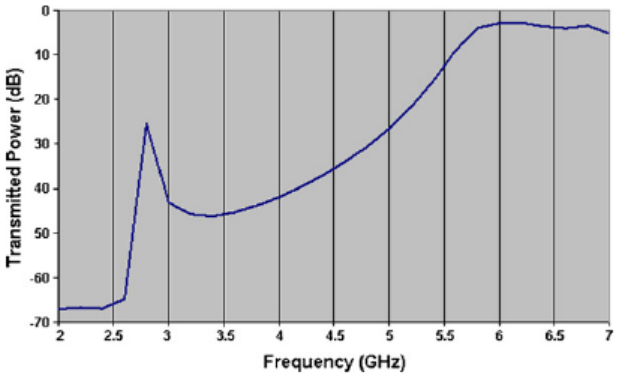

Fig. 2: Modeling results for transmitted power as a function of incident microwave frequency for 2-D lens.

PEPTIDE MICRO/NANOSTRUCTURES AS A PLATFORM FOR DETECTION OF UREA

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Micro/Nanomaterials open new perspectives towards the construction of original devices endowed of unprecedented physicochemical properties. Nevertheless, one of the major challenges for the so-called nanotechnology is the effective use of the functional nanoscale properties and their reproducibility. In the context of this new class of materials, peptides represent one of the most versatile molecular building blocks owing to their rich chemical diversity, inherent ability to interface with biological systems, good physical and chemical stability and ease of preparation. Thus, these materials can be applied in biomedicine, tissue engineering, controlled drug delivery and in biosensing.[1] In this work, we present an electrochemical study of peptide-based device for detection of urea oxidation. Peptidic microstructures - namely, L-diphenylalanine compounds - were used to develop the architecture. The short aromatic homo-dipeptides were used to build the supramolecular assemblies *via* the solid-phase approach recently proposed by Park et al.[2] In the first stage, a peptidic solution was used to form amorphous films onto solid substrates, gold electrodes, previously modified with a self-assembled monolayer of 4-mercaptopyridine. In following, the samples were incubated under an atmosphere satured with the vapor of a second solvent (aniline). The obtained modified electrode show excellent electrocatalytic properties for urea oxydation at 0.1 mol L^{-1} NaOH. Under the optimal experimental conditions, the electrocatalytic response is proportional to the urea concentration in the range of 0.1-1.0 mmol L^{-1}. The sensitivity is calculated to be 56 mA cm^{-2} mol L^{-1} at 0.41 V (vs SCE), which represent a significant advance compared with the typical sensors found in the literature.[3] From our results, we conclude that, even the peptide being an insulating material, this architecture is promissing for use in electrochemical sensors and detection of urea.

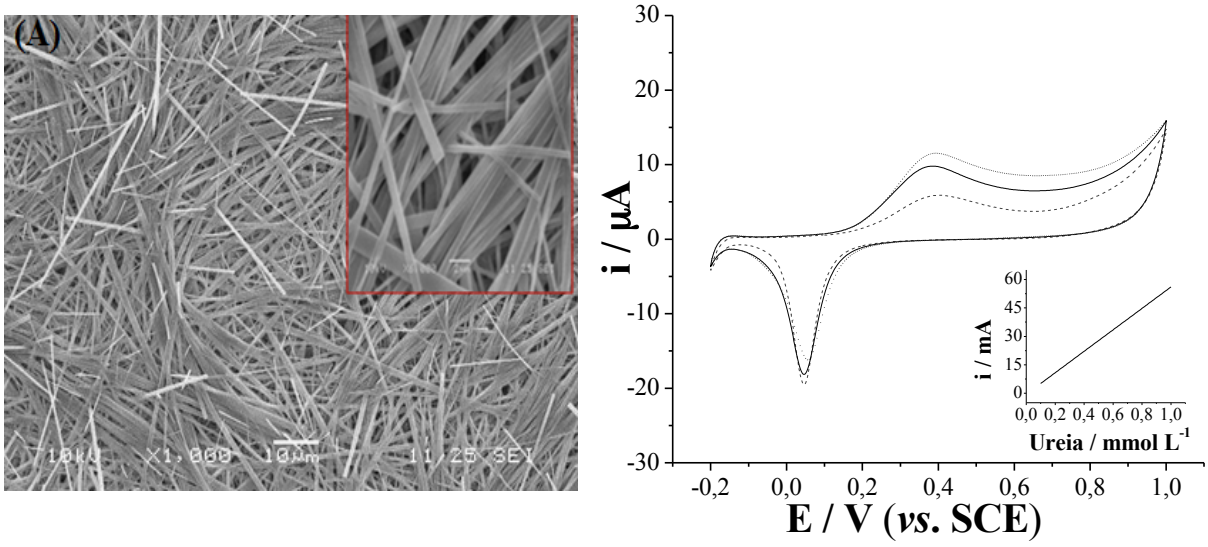

Fig. 1: (A) SEM image showing *L*-diphenylalanine nanostructures; (B) Potential of oxidation of urea for modified electrode with PNTs, without (.....), with 1.0 mmol L^{-1} (——) and 5.0 mmol L^{-1} (- - -) of urea. Electrolyte 0.1 mol L^{-1} NaOH, scan rate 30 mV s^{-1}.

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CHARACTERIZATION OF RETINAL IMPLANTS FOR THE STIMULATION AND RECORDING OF RETINAL CELLS

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Introduction: Retinal implants [1,2] are suited to provide an important approach in neurophysiology for the stimulation and recording of retinal cells with the view to restore or substitute degenerated or dying photoreceptors. They will be an alternative for people suffering from retina diseases such as Retinitis Pigmentosa, and Age-related Macular Degeneration. Retinal implants are used to selectively excite an area of neural tissue in order to generate a pixelated vision.
In this study, we report the fabrication and optimization of retinal implants with parameters such as electrodes geometry and material, that suit best for retina stimulation and recording.
Fabrication process of retinal implants: Initially, a 1.6 µm sacrificial oxide layer was grown on standard silicon substrate and a 10 m layer of polyimide was spun on and cured. Then the metallization layer of platinum (500 nm) for the pad contacts, tracks, and electrodes was sputter deposited and structured using lift-off method. A second 10 µm layer of polyimide was again spun on and cured as top layer insulation. Reactive ion etching (RIE) was used to open contact pads and electrodes and to define the shape of the devices. The devices were released from the wafer by wet etching of the sacrificial oxide layer with a 50% HF solution (fig. 1a).
Results: Electrochemical impedance spectroscopy (EIS) of a platinum [3] retinal implant is given in fig.1b. It shows that platinum has a low double layer capacitance (Cd= 28 µF/cm2, close to theoretical Pt value of 20 µF/cm2) which is an important parameter for recording. Typical impedance range values are around 100-300 k. Such impedance allows signal recording as low as 10 µV at 1 kHz and at the same time contributes to induce a significant stimulation signal. Other characterizations were done like Cyclic Voltammetry or potential window of post processed platinum retinal implants.
Conclusion and Future works: We demonstrated that retinal implants can be manufactured using microtechnology. Electrochemical measurement protocols have been established for the quantification of the electrode-electrolyte interface impedance using EIS. Next steps will be the improvement of the devices using new materials such as PEDOT, graphene, or diamond for their so-called low charge-transfer resistance, and parylene [4] for its higher mechanical and electrical properties compared to polyimide. In-vitro electrical recording and stimulation are also being accomplished.

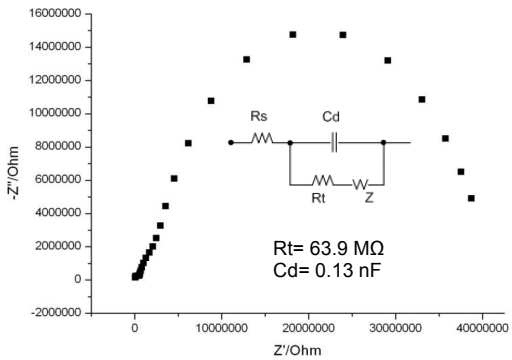

Fig. 1a: (on the left) Head of a retinal implant (electrode diameter: 30 µm);
Fig. 1b: (on the right) EIS of a platinum retinal implant.

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HYBRID DEVICES BASED ON SELF-ASSEMBLED HYDROPHOBIN BIOFILM

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A new family of hybrid organic-inorganic devices can be designed and realized by using biomolecules extracted by natural organisms. DNA single strands, proteins, and enzymes are by far used in many successful applications, mainly in the diagnostic and monitoring fields. Beyond biosensors, biomacromolecules can be directly used to change physical and chemical properties of organic materials. In this communications, we report our newest results about the modification of silicon related surface by using the hydrophobins, small and cysteine-rich fungal proteins produced in the hyphal cell walls.
We have characterized from chemical and optical points of view the self-assembled biofilm of the class I hydrophobin from the fungus Pleurotus ostreatus casted by solution deposition on flat silicon surface and in porous silicon structures. To his aim, experimental procedures and optical models have been developed in spectroscopic ellipsometry, water contact angle, infrared spectroscopy, and atomic force microscopy.
The nanometric biofilm of hydrophobin proteins can protect the silicon surfaces from basic dissolution, such those used in the wet etch processes. Due to the amphiphilic nature of the biofilm, the wettability of silicon surfaces can be turned from hydrophobic to hydrophilic and viceversa. The hydrophobin biofilm can also act as an active substrate to immobilize other biomolecules such as proteins, peptides, enzymes and so on.
The results obtained in the bio-modification of such silicon based surfaces and structures are very promising for the utilization of the hybrid organic-inorganic interfaces in the realization of a new class of microarrays for genomic and proteomic applications.

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A NEW AND HIGHLY SENSITIVE BIOMIMETIC SENSOR FOR HEXAZINONE BASED ON CPE MODIFIED WITH MOLECULARLY IMPRINTED POLYMER

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Molecular imprinting is used for the creation of selective recognition sites in synthetic polymers. In this process, functional and crosslinking monomers are copolymerized in the presence of the target molecule, the template, in a network of organic three-dimensional polymer and considered the footprint as they mimic the biological interaction of antigen-antibody [1]. In this work is presented a new biomimetic sensor based on a carbon paste electrode (CPE) modified with molecularly imprinted polymer (MIP) to monitor the herbicide hexazinone (HXZ) with high sensitivity. This herbicide is used to control a wide variety of broad leaf weeds, grasses, and woody plants [2].

The synthesis of the hexazinone- MIP was performed using the polymerization in bulk. This reaction has been carried out as follows: 0.01 mmol of hexazinone was mixed for 5 min with 0.04 mmol of acrylamide (monomer) in 10 mL of toluene as polymerization solvent. The cross-linker EGDMA (40 mmol) and the initiator (0.4 mmol) of 2-2´-azo*bis*isobutyronitrile were then added to the above solution. The solution was placed under a nitrogen flow for 5 minutes, and then left in a water bath at 60 °C for 24 h, then the polymer was ground, sieved (≤ 180 mm) and submitted to washing in soxhlet for 48 hours with MeOH/CH_3COOH solution 9:1 (v/v) for removal of the analyte. The reference non-imprinted polymer (NIP) was prepared using the same procedure in the absence of the template. The sensor for HXZ was prepared by mixing adequate percentages of graphite powder, mineral oil, and MIP (or NIP), like the recognizer. The electrochemical behavior of the sensor was studied by cyclic voltammetry (Fig. 1b) and the HXZ quantification (Fig. 1a and inset in 1c) was carried out using differential pulse cathodic stripping voltammetry (DPCSV) [3]. For this, a procedure of three steps was followed: (*i*) analyte accumulation; (*ii*) electrode washing and (*iii*) HXZ quantification using DPV. Under these conditions, was obtained a response range for HXZ from 5.1 x 10^{-12} up to 1.6 x 10^{-11} mol L^{-1}; and a detection limit of 1.7 x 10^{-12} mol L^{-1}.

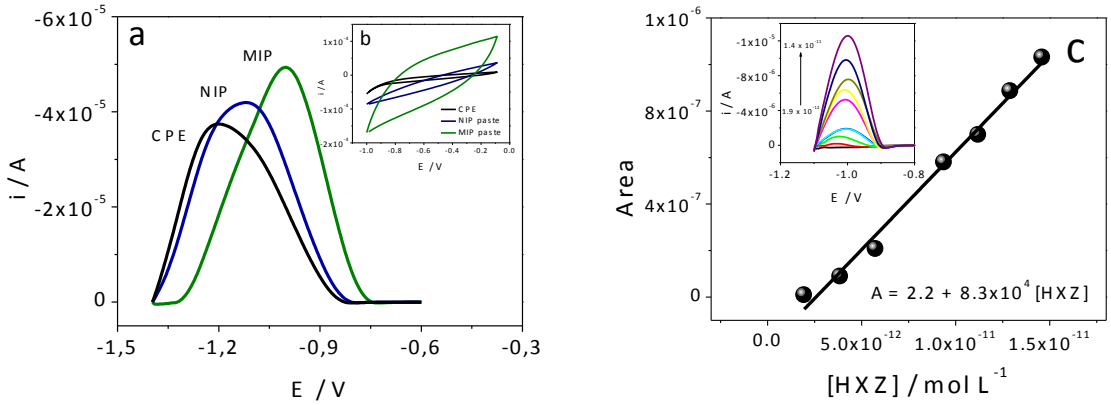

Fig. 1. (a) DP voltammograms of 1.0 µM of HXZ at the surface of MIP, NIP and CP electrodes. Measurement conditions: HCl 0.1 mol L^{-1} pH 2.8, E_{ac} = −0.5 V, t_{ac} = 200 s. (b) Cyclic voltammograms of 150.0 µM of HXZ at the surface of MIP, NIP and CP. Measurement conditions: HCl 0.1 mol L^{-1}, pH 2.8, scan rate = 50 mV s^{-1}. (c) Calibration curve for HXZ with MIP-CPE by using DPCSV and inset the DPCS signals. Measurement conditions: HCl pH 2.8, t_{ac} = 200 s, E_{ac} = −0.5 V, scan rate = 50 mV s^{-1}, pulse amplitude = 100 mV

The results obtained showed that the proposed sensor is promising for the sensitive quantification of HXZ. In addition, further experiments are carried out in order to evaluate the selectivity and real application of this new biomimetic sensor.

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A Bi-Ligand Co-Functionalized Gold Nanoparticles-Based Calcium Ion Probe and its Application to the Detection of Calcium Ions in Serum

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Calcium ions are essential for regulating numerous biological processes such as excitability, neurotransmitter release, gene transcription, cell proliferation, synaptic plasticity, and hormone secretion.[1] Recently, colorimetric probes for calcium ions have been developed using AuNPs functionalized with oligosaccharide and calsequestrin, respectively, and AuNPs stabilized with cytidine triphosphate.[2-4] Oligosaccharides are well-known to chelate Ca^{2+} ions and the interaction enhances the oligosaccharide–oligosaccharide interaction. This property has been used to develop AuNP-based colorimetric probes to detect Ca^{2+}.[5] However, these probes exhibited interference from the presence of Mg^{2+} ions and low sensitivity in mM ranges. We speculated that these problems can be solved by introducing a combination of carboxylic acid and oligosaccharide groups into AuNPs. We selected AuNPs functionalized with a 2 : 1 ratio of 1-thiohexyl carboxylic acid and 1-thiohexyl β-D-lactopyranoside as a Ca^{2+} probe. This probe was highly selective for Ca^{2+} ions over other metal ions relevant to blood serum and it allowed assay of the Ca^{2+} ions up to 1.9 μM. Moreover, the probe determined Ca^{2+} concentrations in various serum samples and the results correlated well with those obtained by using ICP-AES.

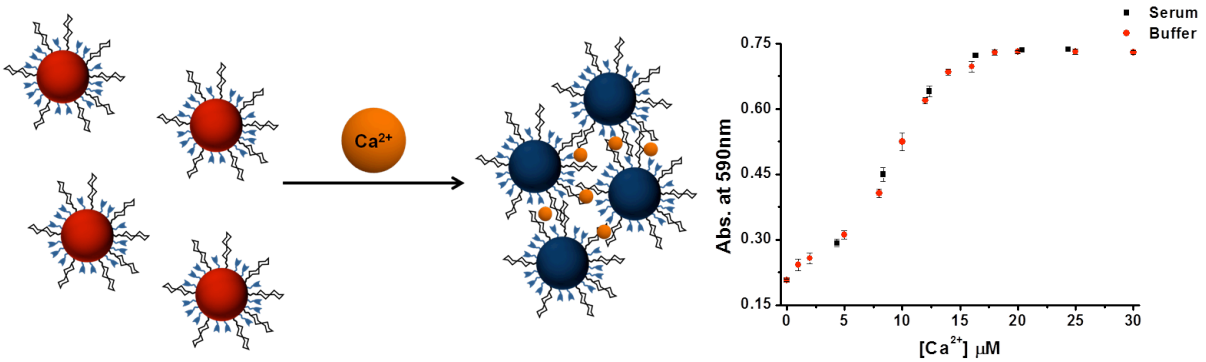

Fig. 1: Schematic illustration of AuNPs aggregation in the presence of Ca^{2+}

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ELECTROCHEMICAL DNA NANO-BIOSENSOR FOR THE STUDY OF CIPROFLOXACIN–DNA INTERACTION

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The study of the interaction of DNA with small molecules such as drugs, organic dyes and metals has been an intensive topic for decades because it provides insight into the screening design of new and more efficient drugs targeting to DNA, which can speed up the drug discovery and development processes [1-4].

In this work we described the interaction of ciprofloxacin (CP), an antibacterial drug, with double stranded DNA (dsDNA) by cyclic voltammetry. The electrode (MWCNT/GCE) exhibited excellent electrocatalytic behavior for the oxidation of CP as evidenced by the enhancement of the 2e-oxidation peak current and the shift in the anodic potential to more negative potential in comparison with a bare GCE. In the presence of DNA, the oxidation peak current of CP decreases and the peak potential shifts to a positive potential (25mV) which indicated the interaction of CP with DNA. Cyclic voltammograms of CP recorded from pH 2–10. With the increase of pH of the solution, the peak potentials shifted to less positive values. According to the plot of the peak potential vs. pH, CP has two pKa values as 6.0 and 7.3. The formal potential with pH showed a slope of -55 mV per unit of pH, close to the anticipated Nernestian value of -59 mV for a two-electron and two-proton processes. The anodic peak current of CP was proportional to the scan rate, which indicates that the electrode process is surface-controlled. The transfer coefficient (α) and standard rate constant of the reaction (k_s) were calculated according to Laviron equation for the DNA/MWCNT/GCE. According to the Langumuir adsorption thermodynamic equation the Langmuir adsorption constant of CP at DNA/MWCNT/GCE was determined as 2.39×10^3 M^{-1}.

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NON-IONIC SOLID POLYMERIC RESIN AMBERLITE XAD-7 DOPED WITH A SELECTIVE FLUORESCENT DYE AS SENSING MATERIAL FOR DETECTION OF IODINE

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A butenolide derivative, 5-Hydroxy-7-(thiophen-2-yl)-3-(trimethylsilyl)-5-[3-(trimethylsilyl) prop-2-ynyl]-5,6- dihydrobenzofuran-(4H)-2-onethe (dye) has been applied as a novel fluorescent probe for the development of a robust optical sensor for iodine. The response of the sensor is based on fluorescence quenching of the dye by iodine in a flow injection system. The fluoresencet dye was characterized spectroscopically and showed an excellent photostability, and high luminescence quantum yields. A non-ionic solid polymeric resin, Amberlite XAD-7 was selected as solid support for efficient immobilization of the fluorescent dye. The experimental parameters were investigated to select the optimum operating conditions. After each measurement, the solid support is efficiently regenerated by injecting 1.0 ml of thiosulfate 0.05 M into the flow system. The calibration graph obtained showed a positive deviation from linearity in the simple Stern-Volmer plot but well fitted by the modified Stern-Volmer equation. A detection limit of 0.5 μg ml^{-1} for iodine was achieved for 2-ml sample injection. In addition to its high stability, repeatability, reversibility, and long working lifetime, the optical sensor revealed good selectivity for iodine over several common diverse ions.

INSPIRED BY PROTEINS AND INORGANIC MATERIALS INTERACTION: APPLICATION OF ASBESTOS-BINDING PROTEINS TO QUICK ASBESTOS MONITORING

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Peptides and proteins have been selected as an affinity reagent to inorganic materials by using a combinatorial biological protocol, such as bacterial cell surface and phage-display technologies. These peptides and proteins were applied to control inorganic crystal growth and nanoparticle assembly, but not so far used as specific detection of inorganic materials. Here we discovered asbestos-binding proteins and applied them to quick asbestos monitoring.

Asbestos is a fibrous silicate mineral that has been used for acoustic and thermal insulation, as a fire retardant, and for other aspects of building because of its chemical and thermal stability. Asbestos is made up of microscopic bundles of silica fibers that can become airborne when damaged or disturbed. Inhalation of asbestos can cause serious health problems. Although the World Health Organization has classified asbestos as a human carcinogen, it remains common in most of the world and the incidence of asbestos-linked pleural mesothelioma and other lung cancers due to asbestos inhalation continues to rise.

There are several types of asbestos, which differ in chemical composition, fiber shape, and toxicity. Chrysotile ($Mg_6Si_4O_{10}(OH)_8$), a serpentine fiber, accounts for more than 90% of industrial asbestos. Amosite ($(Fe, Mg)_7Si_8O_{22}(OH)_2$) and crocidolite ($Na_2(Fe^{3+})_2(Fe^{2+})_3Si_8O_{22}(OH)_2$) are rod-like, durable amphibole fibers that are linked to higher risks of pleural mesothelioma. Having accurate techniques for measuring asbestos levels and identifying its type is critical for determining the extent of asbestos contamination and its health risks. A number of methods have been developed to assess asbestos contamination using microscopy and X-ray diffraction. Phase contrast microscopic analysis is a simple and fast method to observe asbestos, but it is difficult to distinguish asbestos and non-asbestos fiber. Furthermore, there are many smaller fibers that can not be visualized under microscopy. Electron microscopic analyses are able to detect smaller fibers and identify the types of asbestos fiber, but they are tedious and require special skills for handling.

Recently, we discovered that bacterial protein DksA binds to chrysotile specifically. We developed a convenient colorimetric assay for chrysotile using a fusion of DksA and alkaline phosphatase along with 5-bromo-4-chloro-3-indolyl-phosphate and nitro blue tetrazolium as substrates. This colorimetric assay toward building materials used to cover walls and ceilings showed that chrysotile contents are comparable to those obtained with the conventional X-ray method. The detection limits were as low as X-ray diffraction method (0.1% chrysotile in the materials).

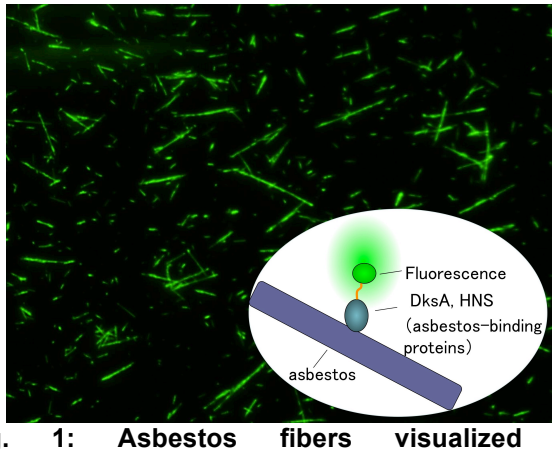

Fig. 1: Asbestos fibers visualized by fluorescently-labeled asbestos-binding proteins under fluorescent microscopy.

To detect airborne asbestos fibers, we developed a fluorescence microscopy-based method (FM) for selective and highly sensitive detection of two different types of asbestos. We also found bacterial proteins that can bind to amphibole asbestos. This method relies on multicolor staining of the asbestos fibers collected on the filter membrane using fluorescently-labeled DksA and amphibole-binding proteins. The diameter of the thinnest asbestos fibers visualized using the FM platform was 30-35 nm. With a portable fluorescence microscope, our method could be used for on-site quick monitoring of airborne asbestos, for example during demolition work. Our method allows simple, speedy, selective and highly sensitive detection of all asbestos types, which is sufficient for routine asbestos monitoring.

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INVESTIGATION ABOUT INTERACTION OF BIOMIMETIC POLYMER WITH THE BASIC RED 9 DYE USING AFFINITY ISOTHERM

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Molecularly imprinted polymers (MIPs) can be consider artificial biological receptors, such as antibodies, and are produced by growing a polymer around a template molecule (analyte). Once the polymer has formed, the template is removed and molecular holes remaining are specific in size and shape to the template. Upon rebinding of the target molecule, a measurable signal is produced that can be quantified. MIPs offer high specificity and selectivity to the molecules that are used for their formation [1]. This paper presents the study of interaction between the MIP and the basic red 9 (BR9) dye using computer simulation to found the monomer which has better interaction with the analyte and verification experimental of the dye affinity with the corresponding MIP by the study of affinity isotherm.

The simulation was used to obtain information about the affinity between the dye and the 20 commercially available monomers. For this, the following software's were used: HyperChem® 8.0.5, OpenEye®, AutoIt 3.3.6.0, Multiple Minima Hypersurfaces (MMH) with MOPAC (Molecular Orbital PACkage) 2009. The synthesis of MIP was performed using the polymerization technique in bulk. This reaction has been carried out in test tubes of 50 mL, as follows: 0.02 mmol of BR9 dye was mixed with 1 mmol of acrylonitrile (monomer), 10 mL of methanol (solvent), 40 mmol of ethylendimethacrylat (EDMA – cross-linker) and 0.4 mmol of 2-2´-azobisisobutyronitrile (AIBN – radical initiator). The solution was placed under a nitrogen flow for 5 minutes, and then the tube was sealed and left in a water bath at 60 °C for 24 hours. The polymer solids formed were to stand for 24 hours at fume hood by evaporation of residual solvent and, finally, they were ground, sieved (≤ 180 mm) and submitted to washing in soxhlet for 48 hours with 100 mL of methanol and acetic acid solution 9:1 (v/v) for removal of the analyte [2]. A control polymer (NIP) was synthesized exactly as where the MIP, except for the addition of the template molecule in the reaction system. For the construction of curves isotherms, 5 mg of the MIP and NIP was added to 3,0 mL of aqueous solution of the analyte in 5 mL vials sealed at different concentrations: 0, 10, 50, 100, 250, 500 mg L^{-1}. These solutions were kept under stirring for 12 hours at room temperature [3]. Then the solutions were filtered and 228nalysed using a spectrophotometer UV/Vis.

Using the computer simulation, it was found that the acrylonitrile is the monomer which presents the best interaction with the BR9 dye. As this computational process is already well diffused in our research group and has shown promising results, only this monomer was 228nalysed. The isotherm curves (Fig. 1) show that the adsorption of MIP and NIP increased with increasing of BR9 concentration. The MIP adsorption was higher than that of the NIP, which indicates that the cavities formed in the MIP recognize and have affinity with the analysis dye. The next steps will provide analysis of isotherms through the synthesis of MIPs for other dyes and application of MIP with better efficiency in optical fibbers to develop a sensor for dyes.

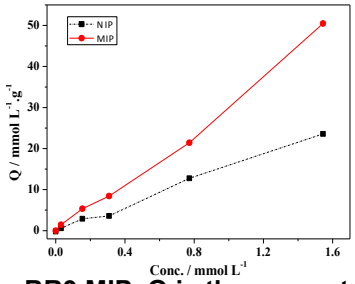

Fig. 1: Binding isotherm for the BR9 MIP, Q is the amount of BR9 bound to 5.0 mg of the respective polymer; V = 3.0 mL; binding time: 12 h.

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STUDY AND APPLICATION OF A SCREEN-PRINTED BIOMIMETIC SENSOR MODIFIED WITH MWCNT IN THE ELECTROCATALYTIC OXIDATION OF THIRAM

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Biomimetic sensors based on the use of artificial redox enzymes have been used to develop more stable and durable amperometric detectors. Compared to biosensors, advantages of these devices include better availability and stability, as well as lower cost. They offer improved electron transfer between the electrode/active site (biomimetic catalyst/substrate) [1], while maintaining the selectivity shown by enzymatic systems. A further advantage is that the signal obtained using biomimetic sensors is direct, rather than derived from an inhibition relationship. All the P450 enzymes contain a common active site, iron protoporphyrin IX, which catalyzes numerous chemical reactions in organisms, usually producing metabolites that are physiologically essential or beneficial [2]. A viable procedure to mimic the P450 active site is to use compounds derived from porphyrins and phthalocyanines of iron or other metals.

A biomimetic sensor based on a screen-printed electrode modified with cobalt phthalocyanine (PcCo) and multi-walled carbon nanotubes (MWCNT) was developed as a reliable alternative technique for the sensitive and selective analysis of the thiram fungicide.

The sensor was electrochemically characterized using cyclic voltammetry and analytically optimized by amperometric technique (Fig. 1A). The best amperometric responses were obtained at 800 mV *vs.* Ag/AgCl(KClsat), using 0.1 mol L^{-1} phosphate buffer solution at pH 8.0 (inset Fig. 1A). In order to improve the detectability of the sensor, the square wave voltammetry (SWV) was used for thiram quantification. Therefore, using the SWV was obtained a response range for thiram from 4.9 x 10^{-6} up to 2.4 x 10^{-5} mol L^{-1}; sensitivity of 2.5 x 10^{5} µA mol L^{-1} and limits of detection and quantification of 1.5 x 10^{-6} and 4.9 x 10^{-6} mol L^{-1}, respectively (Fig 1B).

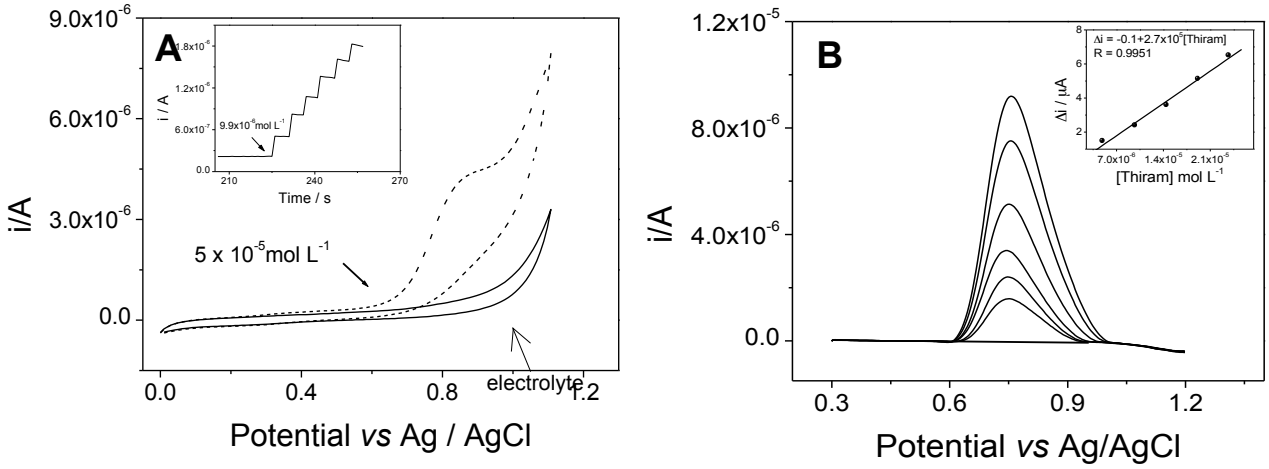

Fig. 1: Profile of voltammetric and amperometric responses of the proposed sensor (A); and square wave voltammograms obtained for different concentrations of thiram. Measurements in 0.1 mol L-1 phosphate buffer (pH 8.0). For SWV was used frequency of 10 Hz, A of 100 mV and ΔEs = 10 mV.

The results showed that the presence of the mediator and MWCNT incorporated into the sensor was essential for increased sensitivity and selectivity. The device has been demonstrated to be suitable for analyses involving environmental matrices

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STIMULI-RESPONSIVE PHOTONIC CRYSTAL MEMBRANES FOR OPTICALLY ENCODED SENSING

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The development of sensing techniques is driven by the ever increasing demand for miniaturized sensing platforms with fast response in areas such as bioassays, environmental monitoring and disease diagnostics.[1] Among the various kinds of sensing architectures, photonic crystal (PC) sensors that employ stimuli-responsive materials as signal transducers have been demonstrated to be promising in that they are able to perform sensitive detection in a non-destructive and label-free way.[2] Herein, a versatile photonic crystal sensing motif based on a two-dimensional (2D) inverse opal monolayer of stimuli-responsive polyelectrolyte gel with tunable optical properties is reported.[3] The photonic membrane shows prompt and reversible response to pH and can be readily read out from either its optical spectra or interference colours (Fig. 1).

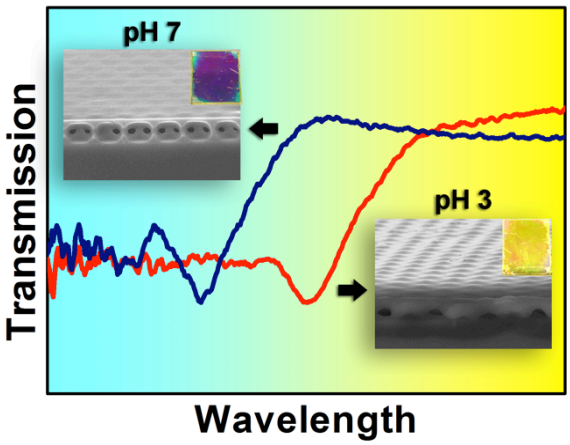

Fig. 1: Structural and colour change of the photonic crystal membrane in response to pH.

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MODELLING COMPLEX BORON TRANSFER KINETICS IN STRONGLY DOPED P+ POLYSILICON / NITROGEN-DOPED-SILICON BI-LAYERS GATES

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Keywords: Boron, Nitrogen, Complex Redistribution, Silicon, Bi-layers, Activation anneal.

The strongly doped P^+ polycrystalline-silicon is a key element of today's advanced very-large-scale-integration (VLSI) technology. To continue scaling down P^+ polysilicon gates of metal-oxide-semiconductor (MOS) integrated circuits, it is necessary to create very shallow junctions with strong-concentrations of electrically active boron (B). Two related processes limit the realization of this goal: (i) the transient enhanced redistribution of the B during the thermal dopant-activation annealing, which causes B penetration through thin oxides from the P^+ polysilicon gate into the underlying layers, and (ii) the formation of electrically inactive B clusters and B precipitates, which decreases the dopant activation rate. The use of low-energy doping methods, co-doping techniques, low thermal annealing temperatures, short annealing times, amorphous-silicon layers, and thin nitrogen-doped-silicon (NiDoS) layers have been practiced to avoid the doping depletion of P^+ polysilicon gate at the oxide interface. Currently, significant research efforts are focused on improving the B activation; problem common to all the practiced methods and techniques.
In this work, based on the approach of using thin bi-layers gate, we investigate NiDoS layers for reducing B enhanced redistribution or gate depletion and for improving B activation. Fast B transfer is reduced by increasing nitrogen atoms. The goal is to develop a fundamental understanding about the complex B transfer process into strongly in-situ doped P^+ polysilicon / NiDoS bi-layers.
We study the instantaneous kinetics of B redistribution, transfer, clustering and segregation around the bi-layers interface during the B activation annealing. The bi-layers have been obtained by low pressure chemical vapor deposition method at 480°C. To avoid long redistributions, thermal annealing was carried out at relatively low-temperatures (700 and 850 °C) for various times ranging between 15 minutes and 2 hours. The doping profiles of strongly B doped polycrystalline silicon have been obtained by secondary ion mass spectroscopy (SIMS) technique. In order to reproduce the measured SIMS profiles, a redistribution model well adapted to the particular structure of bi-layers and to the effects of strong-concentrations has been established. This model is given by two coupled continuity equations for two dopant populations regions. The total B population is divided between the poly-Si region and the NiDoS one, coupled together by instantaneous effective B transfer or exchange between the two regions (named a two-stream transfer process). Five transport mechanisms for B-atoms have been considered: (a) effective transfer in poly-Si region, (b) effective transfer in NiDoS region, (c) effective segregation near the poly-Si / NiDoS interface, (d) clustering effects in the two regions, and (e) peak concentration appearance and evolutions or motions. Moreover, effects of strong B concentrations such as that of the internal electric field influence, the charged vacancies influence, and the solubility solid limit excess are also considered.
The good adjustment of the simulated profiles with the experimental SIMS profiles allowed a fundamental understanding about the instantaneous physical phenomena giving and disturbing the complex B redistribution profiles-shoulders. The increasing kinetics of the B peak concentration near the bi-layers interface is well reproduced by the established model. Strong-concentration B will lead to the formation of small clusters that enhances the B transfer. This enhancement diminishes with the clusters evolution during annealing.

CORROSION AND ELECTROCHEMICAL BEHAVIOUR OF ALUMINIUM TREATED BY TWO TECHNIQUES OF ANODISATION

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In this study, the anodic alumina was produced by two type anodising process (conventional anodisation and double anodisation) in 1 M sulphuric acid at constant cell potential of 25 V. The temperature was kept constant at 5°C during both anodising processes. Anodised samples exposed to 0.2 M K_2SO_4 solution for up to 24 h have been studied by means of electrochemical impedance spectroscopy (EIS). The results reveal that the EIS technique is a good tool for obtaining detailed information on the influence of the ageing process on anodised aluminium. Potentiodynamic polarization tests were conducted to assess the corrosion resistance of the coatings. Measurements of polarization resistance show that a double anodising process confers on material a clear improvement with corrosion in very aggressive medium. The analysis was completed with the aid of the SEM. It was found that the modified anodising, an environmentally friendly coating method, could produce an oxide coating with good corrosion protection for the Al–Mg alloy.

CYCLIC VOLTAMMETRY STUDIES OF NANOSTRUCTURED ACTIVATED CARBON FROM A POSIDONIA OCEANICA USED IN ELECTROCHEMICAL CAPACITORS

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Keywords: Activated carbon, posidonia aceanica, supercapacitors, galvanostatic charge/discharge, electric energy storage.

Electrochemical capacitors are charge-storage devices, which possess higher power density and longer cycle life than batteries. In this paper we realized the synthesis of activated carbon starting from a posidonia aceanica and applied as electrode for supercapacitor, and characterized by adsorption methods by Brunauer-Emmett-Teller (BET) and Barrett-Joiner-Halenda (BJH), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The electrochemical characterizations of the electrode (AC) in H_2SO_4 electrolyte were carried out by galvanostatic chronopotentiometry (GCP) where the specific capacity during charging / discharging is 127 F g-1 and by cyclic voltammetry (CV) for an overtension of 1.3 V / SCE, showed that the material behavior is purely capacitive. It has been found that the electrode has excellent electrochemical reversibility.

STRUCTURAL INVESTIGATIONS OF THE ACTIVE LAYER OF PHOTOVOLTAIC SYSTEMS

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Ever since porphyrin-fullerene dyad [1] composed of fullerenes (acceptors) and porphyrins (donors) had been successfully synthesized and investigated for the first time, they had attracted a considerable attention of the researchers as efficient molecular systems for photoinduced charge separation. For practical use in photovoltaic devices and biochemical sensors the dyad molecules must be organized into layer structure with the uniform orientation order of donor-acceptor pairs. A convenient method of obtaining such organized structure is Langmuir-Blodgett technique. The concept of constructing and synthesizing was developed for the samples of porphyrin-fullerene dyads with double bond, and self-organization into monolayers with uniform orientation of porphyrin and fullerene moieties on the surface of liquid [2, 3].

The aim of this study was to investigate of orientational properties of porphyrin-fullerene dyads in order to optimize the process of forming monolayers of functional substances in the manufacturing technology of advanced organic photovoltaic devices.

The monolayers of porphyrin-fullerene dyads (TBD6a, ZnDHD6ee, DHD6ee) were formed on the surface of water subphase and transferred onto a solid substrate by Langmuir-Schaeffer method. The structures of isolated molecules and their packing in accordance with the data of area per molecule isotherm were built using computer modeling methods.

The research of structural properties of molecular films on the substrate had been done by X-ray reflectometry method. Orientational properties of dyads were studied by X-ray standing waves method in the region of total external reflection. The crystal structure of organic monomolecular films was studied by electron diffraction.

The experimental data had been compared with the results of molecular modeling of the single molecules, to clarify the structure of monolayers and modeling of electronic properties of the investigated systems.

As a result of the research the data on structural properties of monolayers of porphyrin-fullerene dyads were obtained. The thickness of the monomolecular layers and the orientation of organic molecules on the surface of the solid substrate was determined. An analysis of the diffraction patterns showed also that 3D microcrystallites can be formed in some regions of films during their transfer. It is shown that the deposition of the monolayer onto a silicon substrate inherits dyad orientation on a water subphase surface, that is in good agreement with the photovoltaic response of such structures [3].

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ENHANCING ELECTROCHEMICAL PERFORMANCES OF LITHIUM ION BATTERY USING MESOPOROUS $Li_3V_2(PO_4)_3$ /C MISCROSPHERES

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Very recently, we have established an approach, by which we are able to prepare advanced mesoporous materials(e.g., TiO_2, hollow cuprous oxide microspheres, mesoporous zirconium phosphate, mesoporous zinc phosphate nanoparticles and mesoporous hydroxyapatite) using yeast cells as biotemplates under ambient conditions.[1-5] *Mesoporous $Li_3V_2(PO_4)_3$–carbon (LVP-C) microsphere is also synthesized using Baker's yeast cells as both mesoporous structure templates and amorphous carbon sources.*[6] *These microspheres are composed of nanoparticles (20~40 nm) as well as nanopores (22.5 nm). The carbon network (16.4 wt.%) on the surface of the $Li_3V_2(PO_4)_3$ nanoparticles facilitates electron diffusion. They have high discharge capacity (about 126.7 mAh g^{-1}), only 2% capacity loss of the initial value at the 50th cycle at the current density of 0.2 C, and high rate capacity of 100.5 $mAhg^{-1}$ at 5 C in the region of 3.0—4.3 V. The apparent Li^+ diffusion coefficient is found to be 6.76×10^{-10} cm^2s^{-1}. The microspheres could be an ideal cathode-active material that fulfills the requirements of rechargeable lithium batteries for high power applications.*

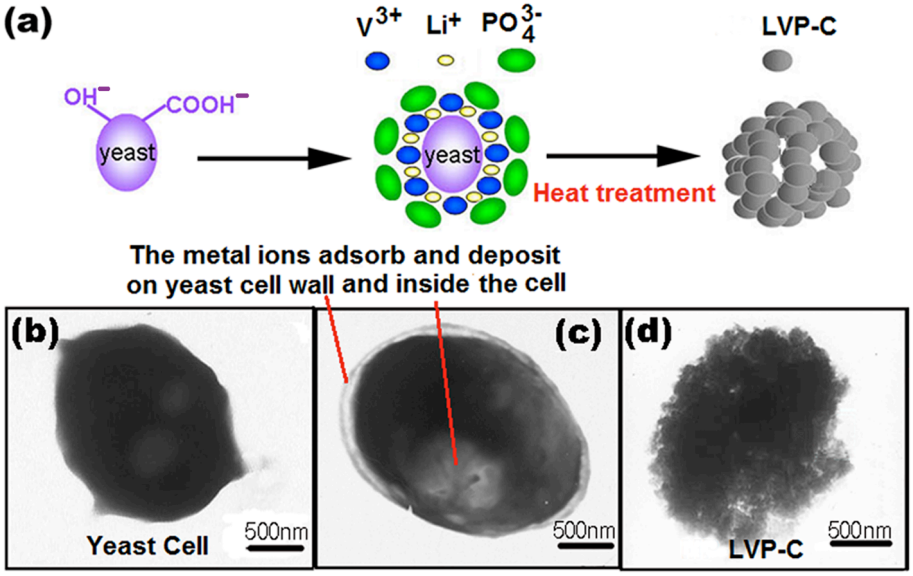

Fig. 1: Formation mechanism of mesoporous microsphere of $Li_3V_2(PO_4)_3$ with amorphous carbon (LVP-C). (a) Schematic drawing of the stucture templating mechanism of biomimetic mineralization process of LVP-C. (b) TEM image of living yeast cells. (c) TEM image of yeast cell after adding Li^+ VO^{2+} PO_4^{3-} into the bioemulsion. (d) TEM image of LVP-C.

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FABRICATION OF LITHOGRAPHY-FREE SILICON SUB-MICRO-PYRAMIDS

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Silicon nanostructures have attracted much attention in recent years because of their unusual quantum properties and potential application (1,2).In the past decade, numerous interesting silicon nanostructures, such as porous silicon (PS)(1) , nanopillars (3), nanorods (4) , and nanowire p-n junction diodes (5),..etc have been developed by various traditional or newly invented methods, and a lot of unique optical or electrical properties were obtained , but the space remained for constructing and developing novel silicon nanostructures is still tremendous.
In this work we report fabrication of ordered arrays of submicron-scale silicon pyramids by simple electrochemical etching of a p-type silicon substrate through Pd deposition. The Pd was deposited on Si substrate by evaporation technique through a mask. The transfer of a hierarchical structure array of Pd masks to the silicon substrate could be achieved by the selective electro-chemical etching of the exposed silicon surfaces in HF/organic solution, which were located in interspaces among adjacent Pd deposited. The morphology and dimensions of the silicon pyramids were controlled by the electrochemical etching parameters (current density, etching time...).Then; inverted pyramids have been formed after long etching times (> 20 min).
Finally, total reflectance spectra show a low reflectance value < 5 % in the visible region. Such result would be very interesting for both solar cells and optical filters applications.

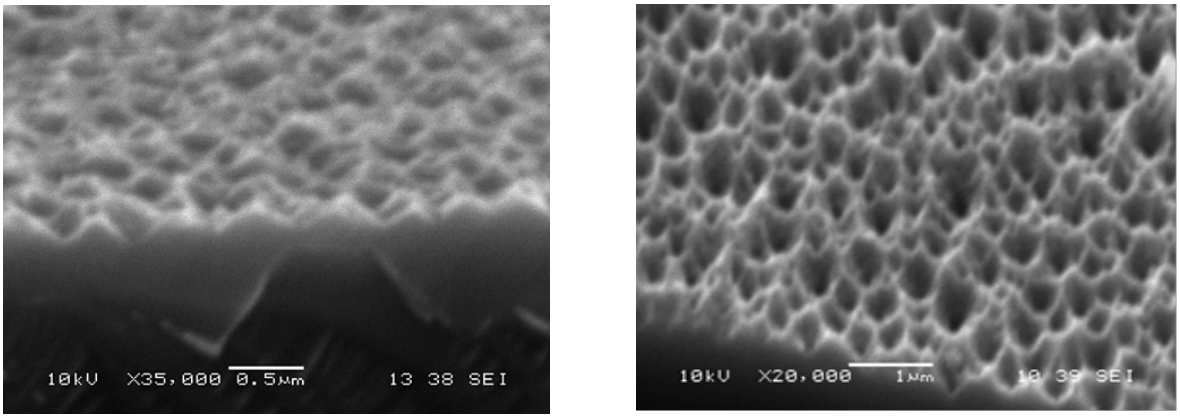

Fig. 1: Scanning electron micrograph (SEM) images of a surface Si/Pd electrochemical etching (HF/organic solution)

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EFFECT OF ETHANOL ADDING ON THE TEXTURE ETCHING OF MONOCRISTALLINE SILICON SURFACE WITH SODIUM HYPOCHLORITE

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The anisotropic etching of monocristalline silicon is often used in the processing of silicon devices [1]. In the fabrication of solar cells, silicon wafers are generally etched in an anisotropic alkaline solution. Pyramidal structures are then formed on the surface to reduce the reflection loss from the front surface. Different etching solutions have been reported in the literature to texture the silicon surface. In the case of monocristalline silicon, mixed alkaline solutions of sodium hydroxide (NaOH) or potassium hydroxide (KOH) with higher concentrations of isopropyl alcohol (IPA) are the most used solutions to texture the silicon surface [2, 3].Other alternative solutions were used to texture the silicon surface such as sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3) and sodium phosphate (Na_3PO_4). Recently, a strong oxidizing reagent NaOCl has been used successfully by several authors to texture the silicon surface [4, 5]. Moreover, NaOCl is cheaper than other etchants and is also largely used in industry. However, the most important inconvenient of NaOCl is its instability, it decomposes in solution. In this work, the effect of the etching parameters such as solution composition, solution temperature on the silicon surface morphology is studied. The surface of etched samples was characterized by Scanning Electron Microscopy (SEM), Spectrophotometry and Secondary Ion Mass Spectroscopy (SIMS). The results clearly show that the presence of ethanol in the solution leads to the formation of pyramids while the absence of ethanol induces the formation of micro-sized cubic structures which evolve to nanowire or nanoneedle structures with etching time. SIMS analysis of these structures indicates that they are mainly composed of Si, O, and Cl.

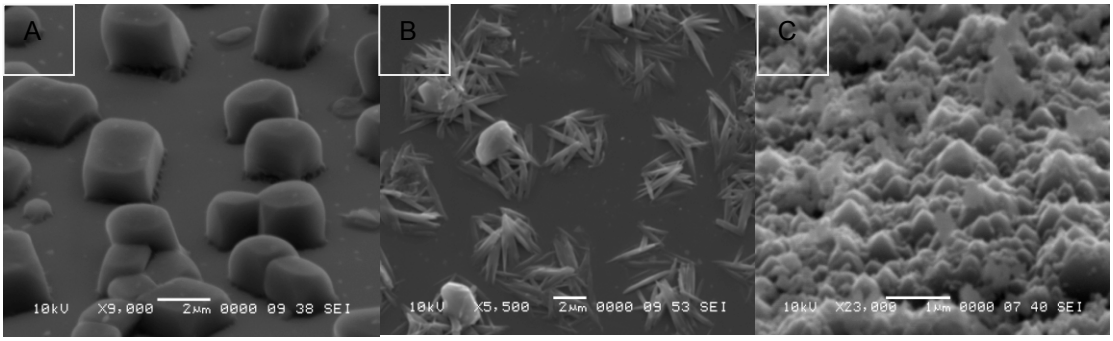

Fig. 1: SEM images of silicon surface etched with NaOCl: (a,b) without Ethanol, (c) with Ethanol

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OXIDE IONIC CONDUCTIVITY OF APATITE TYPE LANTHANUM SILICATES AS AN ELECTROLYTE OF SOFC

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Keywords: Apatite, Lanthanum silicate, Ionic conductivity, SOFC, Impedance spectroscopy.

Apatite silicates have recently been reported as promising electrolyte materials for intermediate temperature solid oxide fuel cells (SOFC) due to its high oxide ion conductivity.
The aim of this work is the synthesis and characterization of a ceramic electrolyte having an apatite structure and general formula $La_{9,33}(SiO_4)_6O_2$.
The sample was prepared with the usual method of solid state reaction, with the starting powders: La_2O_3 and SiO_2. Dense ceramic disk of $La_{9,33}(SiO_4)_6O_2$ with apatite-type structure has been prepared by sintering at 1400°C and then at 1550°C during 3 and 4 hours respectively.
The microstructure and electrical properties of $La_{9,33}(SiO_4)_6O_2$ ceramic are investigated by X-ray diffraction, scanning electron microscopy and complex impedance analysis(determination of: ionic conduction and activation energy). Electrical properties of the sample have been studied between 302 and 802°C by the complex impedance method. Electrical conductivity of this apatite was 3,85 10^{-4}S cm^{-1}at 557 ◦C; it is higher than the ones reported in the literature i.e. 1.13×10^{-4} S cm^{-1}[1] and 7.2×10^{-5} S cm^{-1}[2] for the same material.

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